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The workshop was to provide Technical basis for governmental action on the Kepone contamination problem. It was concluded that investigators must find the source of Kepone contamination, effects of Kepone on biota, and the removal methods for Kepone.

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TABLE OF CONTENTS

ACKNOWLEDGEMENTS/FORWARD 1

LIST OF ATTENDEES 3

WELCOME AND OPENING REMARKS 8

SESSION I: "Monitoring and Current Status of Kepone Pollution Problem"

Kepone Residues in Chesapeake Bay Biota
- M.E. Bender, R.J. Huggett, and W.J. Hargis, Jr. 14

Current Status of Kepone Problem in Maryland
- Donald H. Noren 38

The Current Efforts of Virginia Agencies to Monitor Kepone in the Environment
- Michael A. Bellanca and William F. Gilley 45

SESSION IIA: "Kepone Feasibility Study - Corps of Engineers"

Remedial Measures for Capturing, Stabilizing or Removing Kepone in Gravelly Run, Bailey Bay, and Bailey Creek
- Roland W. Culpepper 67

Environmental Assessment of Engineering Alternatives for Capturing, Stabilizing or Removing Kepone in Gravelly Run, Bailey Bay, and Bailey Creek
- James D. Haluska 106

Potential Dredging Technology on the World Market
- Frank T. Wootton 111

SESSION IIB: "Kepone Feasibility Study - Battelle Northwest"

Current Deposition of Kepone Residuals in the Hopewell, Virginia Area
- Steven J. Shupe and Gaynor W. Dawson 120

Mathematical Simulation of Transport of Kepone and Kepone-Laden Sediments in the James River Estuary
- Yasuo Onishi and Richard M. Ecker 139

Preliminary Evaluation of Approaches to the Amelioration of Kepone Contamination
- G. W. Dawson, J. A. McNeese, and D. C. Christensen 167

SESSION III: "Related Sediment Contamination Problems"

Hudson River - PCB Study Description and Detailed Work Plan
- Edward G. Horn and Leo J. Hetling.................... 185
Hudson River Sediment Distribution and Water Interactions Relative to PCB - Preliminary Indications
- T. J. Tofflemire and T. F. Zimmie.................... 210
The Use of Artifical Substances for Monitoring Toxic Organic Compounds: A Preliminary Evaluation Involving The PCB problem in the Hudson River
- K. W. Simpson, R. C. Mt. Pleasant, and Brian Bush..... 243
Research Progress on Removal or Treatment of PCB in Hudson River Sediment
- P. M. Griffen, A. R. Sears, and C. M. McFarland....... 260

SESSION IV: "Current Research on the Fate and Effect of Kepone"

Effects of Kepone on Estuarine Organisms

- D. J. Hansen, D. R. Nimmo, S. C. Schimmel,
  G. E. Walsh, and A. J. Wilson, Jr. 266
Acute Toxicity of Kepone to Four Estuarine Animals
- S. C. Schimmel and A. J. Wilson, Jr. 283
Kepone Accumulation and Food Chain Transfer
- L. H. Bahner, A. J. Wilson, J. M. Sheppard, J. M.
  Patrick, L. R. Goodman, and G. E. Walsh 294
Fate and Degradation of Kepone in Estuarine Microcosms
- R. L. Garnas, A. W. Bourquin and P. H. Pritchard 330
The Role of Sediments in the Storage, Movement and Biological Uptake of Kepone in Estuarine Environments
- R. Huggett 363
Preliminary Analysis of Kepone Distribution in the James River
- D. J. O'Connor and K. J. Farley 457

SESSION V: "Additional Presentations and Wrap-up"

Remote Sensing Observations of Industrial Plumes at Hopewell, Virginia
- Charles A. Whitlock and Theodore A. Talay 481
Allied Chemical Kepone Investigations
- A. R. Patterson, R. J. Williams, D.E. Scheirer, and
  J. Vitsone.. 502
Summary of Kepone Seminar Issues
- Martin W. Brossman 505

ACKNOWLEDGEMENTS/FORWARD

A second seminar to review the status of the Kepone problem and to exchange technical information was held at the Tidewater Inn, Easton, Maryland. This informal two-day meeting was sponsored by the United States Environmental Protection Agency's Chesapeake Bay Program and the National Marine Fisheries Service of National Oceanic and Atmospheric Administration. The intent of a series of this type is to provide technical basis for governmental action on the Kepone contamination problem.

The first seminar was held at Virginia Institute of Marine Science, Gloucester Point, Virginia in October 1976.

K. K. Wu and Dawn Barboun served as Program Coordinator and Program Assistant, respectively. Success of any project is aided immeasurably by support "from the top." Such support was provided enthusiastically by Jack J. Schramm, Regional Administrator of Region III U.S. EPA and William Gordon, Regional Director of National Marine Fisheries Service.

The ultimate success of this project must be credited to the tremendous effort and direction given by the Seminar Planning Committee. The members of this committee are:

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Of course, the contributions of the Session chairmen and speakers cannot be overestimated. Not only did they present most knowledgeable and timely papers, but they also reviewed the resulting discussions.

Special thanks are due to Muriel Brubaker of National Marine Fisheries Services for managing the registration, to Edward Christoffers and Edward Cohen for arranging the conference's visual aids, and to Gary Gardner for his editorial comments.

The program coordinator and the program assistant regret that it is impossible to retype all papers submitted to us within the time required to publish the proceedings, as it is to identify all of the numerous colleagues and friends who contributed so much to this symposium. We view the dissemination of information on this crucial subject in a timely manner to interested public and scientists, as far more important than the issuance of a "letter-perfect" paper a year later.

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WELCOME AND OPENING REMARKS

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Good morning. I'm Al Morris, Deputy Regional Administrator of EPA in Philadelphia. I'd like to welcome you to Kepone Seminar II.

It seems hard to believe that only a little over two years ago, that the name Kepone was not known at all except to a relatively few people in the pesticide and agricultural field. Today, unfortunately, it's very close to being a household word. Of all the things that have damaged our citizens and our environment, Kepone is one of the worst. Yet, were it not for the gross occupational tragedy which took place at the Life Sciences Product Corporation in Hopewell, we might still not be aware of the danger that Kepone poses to us.

I think that fact bears closer examination. As with Kepone, toxic effects with many chemicals have not become known until some tragedy occurs among the workers who manufacture the product. Because those workers' exposure, even under ideal conditions, is usually higher than the user of the product and much higher than the public in general. Worker illnesses often become a sign of a problem with a chemical product.

There could be many such chemicals as dangerous as Kepone but they still remain unknown because we haven't detected the problem in their manufacturing or with their use.

Toxic chemicals have come to be known as the silent epidemic. An attack on life and our environment whose effect may be delayed by fifteen, twenty, or even forty years, but whose human and economic costs will eventually become quite unacceptable to us.

The World Health Organization has estimated that sixty to ninety percent of all cancer is a direct result of environmental factors. The National Cancer Institute studies reveal a much higher cancer rate in areas surrounding heavy industrial chemical use and activity. Within the last two years, the rate of cancer deaths has increased more sharply than any time since World War II.

Each year we produce approximately thirty thousand different chemical compounds. And annually, approximately a thousand new ones are added to that list. Over the years evidence about the effects of these substances has been accumulating. We know that mercury, lead, cadmium, all can attack the central nervous system. Carbon tetrachloride and chlorinated phenols can damage the liver, and that ethylene glycol and cadmium sulfate can produce kidney disease. We now realize that polyvinyl chloride which was introduced over four years ago, can cause cancer. We have only recently discovered that fluorocarbons can weaken the protective shield of the ozone layer. Asbestos and chloroform have been found in our drinking water and there has been a significant incidence of leukemia in the synthetic rubber industry.

Finally, we come to Kepone. At first it was hoped that Kepone exposure could be found limited to the area immediately around Hopewell. As the investigations continued, we soon found massive environmental contamination by Kepone. The chemical was found in bottom sediments along seven miles of the James River, found in fish in many parts of Chesapeake Bay, and even in the Atlantic Ocean.

Hundreds of men were either put out of work or lost portions of their income due to fishing restrictions in the contaminated areas. Even today there remains a partial ban on fishing in the James River. And I understand that yesterday the ban was extended to portions of the Chesapeake Bay.

It soon became clear that there was a massive lack of information about Kepone. However, to close the information gap, EPA established a Kepone Task Force in August of 1976. The primary function of the Task FOrce is to coordinate the amassing and dissemination of information on Kepone with EPA, and between all federal, state and local agencies. Secondly, to develop and implement a comprehensive action plan to deal with Kepone contamination.

In October 1976, EPA's Chesapeake Bay Program in cooperation with the Marine Institute of Virginia, Institute of Marine Sciences, sponsored the First Kepone Seminar which many of you attended. This was the first opportunity for all agencies, institutions, and persons engaged in Kepone activity, to get together and exchange information.

Some of the findings of the first Kepone Seminar were quite disturbing. For example, food chain studies indicated that non-detectable levels of Kepone in water could accumulate in fish to detectable levels within approximately thirty days.

A great deal of monitoring and research activities have been carried out over the past year in response to the problems raised at the first seminar. We felt that a second Kepone Seminar would be useful to exchange and discuss this new information.

As you know, the EPA and the National Marine Fisheries Service have cooperated in organizing this Kepone Seminar II. I believe that the work we are doing on Kepone should have a much more wide-ranging effect than just discussing Kepone.

Many of the research activities we are undertaking, could be of value in detecting and solving other toxic problems in the future. These new substances fall under the New Toxic Substance Control Act. And they may require studies much as the one we are doing here. EPA now has authority and responsibility to require the testing of new chemicals if our agency feels that they may become potentially harmful to humans or the environment.

I hope the development of that program will hasten the day when there will be no more tragic surprises like vinyl chloride, PCB or Kepone.

With those few remarks, let me welcome you to the Seminar again. And let me express the hope that it is both productive and informative and that you go away feeling that it was worthwhile. Thank you very much.

William Gordon
Regional Director
National Marine Fisheries Service

Ladies and Gentlemen, I'm most pleased to join you here at the Tidewater Inn for this Kepone Symposium. On behalf of the National Marine Fisheries Service, I'm most delighted to welcome you here to the Eastern shore, home of our Oxford Laboratory down the road a bit. I wish also to congratulate the Environmental Protection Agency staff for working with us to put this Symposium together.

I'm sure you will agree that the program arranged by members of eht EPA's Region III staff and by Bob, will be of exceptional value for all of us. Certainly, the Symposium will provide the latest information on the status of Kepone problems in the Chesapeake Bay, the impact of Kepone on the estuarine organisms, and possible remedial measures that should and must be taken. It is imperative that we have this latest information on Kepone, so that proper management decisions can be made affecting the fisheries protection, the estuarine environment, the ready market for our seafood products, and the protection of human health so that we can make these decisions in a prudent and timely fashion.

It was equally important that this information be properly disseminated to the scientists and decision makers concerned with the various aspects on Kepone have the latest information readily available to them. It is imperative likewise that the public be aware of this situation. Society must help to make the decisions regarding our environment.

The purpose of this second Kepone Symposium is to provide public forum to exchange the latest thinking and data on Kepone, to provide an atmosphere for both formal and informal participation.

I'm glad to see that each registrant of this Symposium will be provided with a copy of the proceedings on the second Symposium in the very near future. All papers, extraneous comments made by both speakers and comments from the floor will become part of the permanent record and incorporated into the proceedings.

I feel that the proceedings will be of significant value to all of us. I am hopeful, likewise, that the user groups will use it for public education. I find that public apathy particularly in fisheries management, but also in the protection of the environment, often is based on lack of knowledge. And we owe a great responsibility to the public to make this information available more freely than we have in the past. I'm going to encourage and challenge all of you to do so.

We certainly have a full two days ahead of us. We have much to hear and to learn. You are encouraged to participate in the proceedings. And I look forward to visiting with many of you during the Symposium as possible. I won't be able to stay for the day because as Bob said, I have two more states to make in the district before returning this evening. But I hope to spend all day tomorrow with you and get to know you better. Thank you very much and welcome and good luck on the Symposium.

SESSION I

"Monitoring and Current Status of Kepone Pollution Problem"

CHAIRMAN

Dr. Michael E. Bender
Assistant Director
Division of Environmental Science Engineering
Virginia Institute of Marine Science

SPEAKERS

Dr. Michael E. Bender
"Kepone Residues in Chesapeake Bay Biota"

Dr. Max Eisenberg
Deputy Director
Maryland Department of Health and Mental Hygiene
"Current Status of Kepone Problem in Maryland"

Mr. William F. Gilley
Executive Director
Kepone Task Force
Virginia Department of Health

Mr. Michael A. Bellanca
Deputy Executive Secretary
Virginia State Water Pollution
Control Board

"The Current Efforts of Virginia Agencies
to Monitor Kepone in the Environment"

Kepone® Residues in Chesapeake Bay Biota[1]

by

M. E. Bender, R. J. Huggett and W. J. Hargis, Jr.

Virginia Institute of Marine Science

Gloucester Point, Virginia

September 1977

®Registered trademark for decachlorooctahydro - 1,3,3 - metheno - 2H - cyclobuta (cd) pentalen - 2 one. Allied Chemical Company, 40 Rector Street, New York, New York 10006.

[1] Contribution No. 841 from the Virginia Institute of Marine Science, Gloucester Point, Va. 23062

ABSTRACT

Oysters from the James displayed variations in Kepone residue levels related to water temperature and their spawning cycle. Oyster depuration rates were related to temperature. In summer the "biological half-life" of Kepone in oysters was about one week, while during the winter about 40 days were required for residue levels to decline by 50 per cent. Residues in blue crabs varied as a function of sex, males having considerably higher residues than females. Fin fish levels from the James varied greatly, with residue levels being dependent on species and length of residence for migratory fishes. Average Kepone residues in freshwater fish species, which are resident their entire lives, varied from 0.04 to 2.4 ug/g. Long-term resident estuarine fin fish varied less than freshwater species, with mean concentrations between 0.6 and 2.7 ug/g. Short-term resident marine fish species, e.g. American shad and menhaden, exhibited low residues averaging less than 0.1 ug/g, while spot and croaker, which reside in the river for longer periods, had higher residues averaging 0.81 and 0.75 μg/g respectively.

In the Bay, croaker, spot, trout and flounder all exhibited similar residue patterns showing lower residue levels at stations further up-Bay from the Kepone source in the James River.

Introduction

Kepone, an insecticide whose use in the United States was restricted to an ingredient of ant and roach baits, was produced by two companies located in Hopewell, Virginia between 1963 and 1975. Allied Chemical produced about 1.5 million pounds of the chemical on an irregular schedule between 1966 and 1973. Life Science Products, Inc. made approximately 1.7 million pounds of the insecticide during 16 months of operation in 1974 and 1975. In July of 1975 the plant closed because of inadequate employee protection in the production of the toxic compound.

Effluents from the Life Science plant entered the Hopewell sewage treatment plant and caused its digesters to fail. Since the effluent from the sewage treatment plant was discharged to the upper tidal James River through Baileys Creek (Fig. 1), the U. S. Environmental Protection Agency conducted a survey during the late summer of 1975 to determine if Kepone had contaminated the James River ecosystem. Their report (EPA, 1975) showed the pollutant to be in the air, soil and waters around Hopewell, and since that time extensive monitoring and research activities have been conducted by various state and federal agencies.

This manuscript discusses the results obtained during approximately eighteen months of monitoring Kepone residues in biota from the James River and lower Chesapeake Bay.

Methods

To follow seasonal trends in Kepone residue levels, 12 oysters were taken monthly by the Virginia State Health Department and VIMS from each of the sampling stations shown in Figure 2. To determine depuration rates, oysters were taken from Wreck Shoals in the James River and transplanted to the York and Rappahannock rivers during January of 1975. A similar program was conducted during the early summer when oysters were transplanted to the York from five stations in the James River (Swash Hole, Ballard Marsh, James River Bridge, Pagan River and Nansemond Ridge).

Fin fish, blue crabs and other invertebrates were sampled by trawl over the entire tidal James at approximately 5 mile intervals. In the Chesapeake Bay fin fish collections were made from existing commercial pound nets located as shown in Figure 1. Collections at these stations for five species were made during April, June and September. All collections were either iced or frozen in the field prior to transport to the laboratory for processing.

Clams and oysters were opened at the hinge, drained, shucked, composited, and then blended to obtain a homogeneous mixture. Blue crabs were picked raw and the meats, excluding claw, were combined prior to blending. Fin fish tissues were ground in a meat grinder into hamburger consistency. These samples consisted of either whole fish or fillets (scaled, with skin). Whole fish samples were utilized for small species (less than 30 grams of flesh). The small species included: spottail shiner, bay anchovy, Atlantic silverside, and hogchoker.

Following blending or grinding, all samples were frozen at -5°C for 24 hours in order to rupture cells. After thawing, a mixture of anhydrous sodium sulfate and Quso® G-30 (precipitated silica, Philadelphia Quartz Co.)

was added for desiccation. The proportions of sample to the desiccants were: 30 g mollusk tissue - 81 g $Na_2 SO_4$ - 9 g Quso; 30 g fish or crustacean tissue - 54 g $Na_2 SO_4$ - 6 g Quso. The samples were then mixed and refrozen to insure cell rupture. After thawing, the desiccated samples were ground with a blender to a powdery consistency and transferred to pre-extracted paper thimbles for Soxhlet extraction. Extraction was carried out using 1:1 ethyl ether-petroleum ether for 16 hours. Extracts were then concentrated by evaporation, under vacuum and heat, and cleaned by activated florisil column chromotography (EPA, 1975). The Kepone containing elutriate was analyzed by electron capture gas chromotography utilizing packed columns with one or more of the following liquid phases: 4% SE-30 + 6% OV 210; 1.5% OV-17 + 1.95% QF-1 + 3% OV-1. On occasion, when concentrations and volume were sufficiently large to provide enough material for analysis, Kepone presence was confirmed by mass spectrometry.

Residue concentrations are reported as ug/g (ppm) wet weight.

Results and Discussion

To detect whether differences in residue levels in oysters existed due to sampling location, a one-way analysis of variance was performed on data from 8 stations sampled over a period of 13 months. The overall mean residue level was 0.16 ug/g for this period. Differences between stations were not detected at the 0.05% level (F = 1.70, 7/95 d.f.). Seasonal differences in residue levels were tested by comparing the monthly results from all sampling stations. The F ratio obtained was significant at the 0.01% level (6.48 with 14/101 d.f.). Moving averages were used to construct

Figure 3 which depicts the seasonal variation of Kepone residues in James River oysters. Each point in this figure represents the average of the preceding, present and subsequent months.

In bodies of water contaminated by Kepone, residue levels decline during the colder months, when the oysters are relatively inactive. As feeding increases during the spring, residues increase. A decline in Kepone level occurs after spawning in the late summer and then residues increase briefly until the weather cools when they again decline.

The major value of the oyster beds in the James River is their production of seed oysters which are transplanted to growing areas throughout the entire Chesapeake Bay. Because of this practice and the importance of this seafood to the economy, it was essential to know the rate at which oysters depurated Kepone. Consequently, depuration experiments were conducted.

The results of the depuration experiments are summarized graphically in Figure 4. The loss rate shown during the winter represents the pooled data from oysters depurated in both the York and Rappahannock rivers. These oysters originated from the same stock and were held at locations of similar salinity.

Oysters from five locations in the James were depurated in the York during the summer. The average initial Kepone concentration for these animals was 0.107 ug/g, with a standard error of 0.0023. After 16 days of depuration, the average Kepone concentration for these oysters was 0.018 ug/g with a standard error of 0.0018.

As might be expected, temperature had a dramatic effect upon the rate at which Kepone was depurated by the oysters. In summer the "biological half-life" of Kepone was about one week, while during the winter about 40 days were required for residue levels to decline.

Average Kepone residues for the major species collected in the James River are shown in Table 1. Kepone levels in migratory species, _e.g._ croaker, spot, bluefish, and shad increased as they stayed longer in the estuary; therefore, the residue levels for these species reported in the table are averaged over their period of residence. Residue levels in long-term residents, _e.g._ hogchokers, white perch and catfish, did not fluctuate seasonally. Although the data are limited, no trends in residue levels in the James River could be detected as a function of distance from the Kepone source at Hopewell either for estuarine species or for the freshwater residents.

Considerable variation in Kepone residue occurs between species (Table 1). Freshwater species, which are resident their entire lives, vary in average Kepone residues from 0.04 ug/g to 2.4 ug/g. Of the two species of catfish in the river, which are of major commercial importance, the channel catfish, _Ictalurus punctatus_, and the white catfish, _Ictalurus catus_, the former exhibited lower levels by almost an order of magnitude. We have investigated the total lipid content of these two species (Bligh and Dyer, 1959) as a possible explanation for the residue differences observed and find virtually no difference between the two species in lipid content. The average lipid content of flesh for white catfish was 9.6 mg/g (S.D. 2.3) and 10.7 mg/g (S.D. 2.1) for the channel catfish.

Other possibilities to explain the species differences include either different uptake mechanisms or possibly the existence of metabolic mechanisms for Kepone breakdown and/or elimination in channel catfish which white catfish do not possess.

Long-term resident estuarine (brackish water) fin fish varied less than the freshwater species in their Kepone residues, with average levels between 0.6 and 2.6 ug/g.

Short-term marine fish species, e.g. American shad and menhaden, exhibited low levels of Kepone averaging less than 0.1 ug/g while spot and croaker, which usually reside in the river for somewhat longer periods, had residues averaging 0.81 and 0.75 ug/g respectively.

Blue crab residues averaged 0.19 ug/g for females and 0.81 ug/g for males. The male crabs spend a greater proportion of their lives in the river system than do the females and this habit probably accounts for the observed difference in Kepone body burdens.

Residue levels for other chlorinated hydrocarbon pesticides, e.g. DDT, have been shown to vary as a function of size for a given fish species (Reinhart and Bergman, 1974). We have tested four species of fish (croaker, bluefish, hogchoker and channel catfish) to evaluate whether a similar relationship exists with Kepone. An example of the type of relationship found between Kepone and fish size is shown in Figure 5. Hogchokers, croaker, and bluefish both exhibited similar relationships indicating that Kepone body burdens are not related to the size of the individuals.

The effect of length of residence in the lower James on residue levels can be seen in Figure 6, where a long-term resident, hogchoker, and a migrant, croaker, are compared. Residues in croakers increase as their length of residence increases beginning in January when they first move into the estuary, and increasing linearly throughout the summer. Hogchokers, on the other hand, being permanent residents of the estuary, appear to be at equilibrium with Kepone sources in the river system.

Stations in Chesapeake Bay were sampled for five fin fish species during April, June and September. Our most complete set of data is for 21 June 1976 sampling period, when at least 10 fish of each species were obtained. The results of this survey are shown in Figure 7. Croaker, spot, trout and flounder all exhibit similar residue patterns showing declining residues as one moves up-Bay from the Kepone source in the James River.

Bluefish, however, did not exhibit this pattern--their residues were essentially the same regardless of sampling location. The bluefish, being highly mobile, may move into the James for a time and then migrate to other areas of the Bay mixing with populations which have not stayed in the lower James River for an extended period of time. As a consequence, the resulting population sampled at a given station would be comprised of fishes with both high and low residue levels. Therefore the average residue level does not reflect dilution of the Kepone source, whether food and/or water, as is shown for the other species. Support for this theory is presented in Figure 8 which shows the distribution of Kepone residues in bluefish taken during the late June sampling. As can be seen in the figure, a biomodal distribution pattern exists, supporting our conclusions that those individuals with high residues spent more time in the James, where Kepone occurs, than the somewhat larger group having residues below 0.1 ug/g.

The presence of Kepone residues in aquatic resources of the James River has limited the harvest of certain species and created a situation which may result in damage to the resources through either acute or chronic toxic effects.

Those species in the James River which have body burdens of the pesticide over the established "action levels" may not be harvested. Action levels are established by the Food and Drug Administration when food products are inadvertently contaminated with harmful materials. Since people consume different quantities of various foods, different action levels for different foods are established. The higher action level is assigned to those foods which are eaten in smaller quantities. Present action levels for fisheries products for Kepone are: 0.3 ug/g for fin fish, 0.3 ug/g for oysters and clams and 0.4 ug/g for crabs.

The factors which determine whether a particular species will concentrate Kepone to above the "action level" are not well known. However, we do know that the crustaceans, fishes and shellfish closer to the source, *i.e.* in the James River have much higher residues than those found outside the James.

All commercial fin fish in the James River, with the exception of catfish, shad and herring, exceed the action level of 0.3 ug/g. Male blue crabs in the James generally have levels in excess of 0.4 ug/g, while females caught at the same location have lower residues.

At present we do not have any direct evidence that toxic effects due to Kepone exposure are occurring in the biota of the James River. However, laboratory studies to determine the potential impact of Kepone contamination on some estuarine organisms have been conducted. Hansen, et al. (1977) have shown that the growth of mysid shrimp and sheepshead minnows was reduced by exposure to 0.07 ug/l and 0.08 ug/l respectively. Blue crab mortality was observed by Schimmel and Bahner (1977) during a 28 day feeding experiment when the animals were fed food contaminated with Kepone at levels of 0.15 and 1.9 ug/g. Dupuy (1976) found setting success of larvae produced by Kepone-contaminated oysters taken from the James and spawned in the laboratory to be equal to control groups. Additional studies are in progress to further assess the potential effects of Kepone on other estuarine and freshwater organisms.

The results of two of these studies indicate that effects on populations of some species may be occurring in the James River. The strong probability that blue crab mortalities are related to ingestion of Kepone is indicated by the fact that Kepone residues in most James River fish, a primary food of the crab, are equal to or exceed those which produced mortality in the laboratory. In addition, Kepone residues in James River fish are frequently higher than those reached by laboratory fish populations which were deleteriously affected by Kepone exposures (Hansen, et al., 1977).

The rapid accumulation of Kepone by fishes such as spot and croakers during their spring migrations has demonstrated the continuing availability of Kepone in the system. Although we cannot project future conditions on the basis of scarcely more than a year's data, there is no indication of a significant decline of residue levels in James River animals. Furthermore Kepone is a long-lived chemical species. We must conclude, therefore, that unless the reservoir of Kepone available in the system is somehow reduced, present conditions will continue for many years.

ACKNOWLEDGMENTS

The significant contributions of Harold Slone, Dwight Hunt, Keith Ward and Peter VanVeld in the chemical analysis, and John Merriner, Robert Doyle and Dexter Haven in the animal collections are gratefully acknowledged.

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Hansen, D. J., D. R. Nimmo, S. C. Schimmel, G. E. Walsh and A. J. Wilson, Jr. 1977. Effects of Kepone® on estuarine organisms. Environmental Research Laboratory, Gulf Breeze. Kepone Seminar II, Easton, Maryland, Sept. 1977.

Reinert, R. E. and H. L. Bergman. 1974. Residues of DDT in lake trout (*Salvelinus namaycush*) and coho salmon (*Oncorhynchus kisutch*) from the Great Lakes. J. Fish. Res. Board Can. 31:191-199.

Schimmel, S. C. and L. S. Bahner. 1977. Bioaccumulation of Kepone® from food by, and on its effects on several estuarine animals. Environmental Research Laboratory, Gulf Breeze. Kepone Seminar II, Easton, Maryland, Sept. 1977.

Table 1

JAMES RIVER - KEPONE RESIDUES (ug/g)

Longterm Residents	$\bar{X}$	N	Std. Error of $\bar{X}$
Spottail shiner (Notropis hudsonius)	0.08	6	0.02
Channel catfish (Ictalurus punctatus)	0.04	45	0.004
White catfish (Ictalurus catus)	0.25	14	0.03
American eel (Anguilla rostrata)	0.64	15	0.55
Black crappie (Promoxis nigromaculatus)	1.0	10	0.13
Largemouth bass (Micropterus salmoides)	2.4	14	0.54
White perch (Roccus americanus)	2.7	20	0.39
Bay anchovy (Anchoa mitchilli)	0.65	13	0.15
Atlantic silverside (Menidia menidia)	1.6	15	0.43
Hogchoker (Trinectes maculatus)	0.94	22	0.13
Grass shrimp (Palaemonetes pugio)	0.60	8	0.15
Sand shrimp (Crangon septemspinosa)	2.0	3	0.09
Xanthid crabs	0.27	3	0.03
Blue crab (Callinectes sapidus) female	0.19	180	0.02
Blue crab (Callinectes sapidus) male	0.81	43	0.07
Oyster (Crassostrea virginica)	0.16	140[1]	0.01
Hard clam (Mercenaria mercenaria)	0.09	12[1]	0.009
Short-term Residents			
American shad (Alosa sapidissima)	0.03	50	0.004
Atlantic menhaden (Brevoortia tyrannus)	0.05	8	0.02
Spot (Leiostomus xanthurus)	0.81	40	0.13
Croaker (Micropogon undulatus)	0.75	60	0.16
Bluefish (Pomatomus saltatrix)	0.29	30	0.20

[1] Blends of 12 individuals

Figure Legends

Fig. 1	Location of Chesapeake Bay sampling stations and Kepone discharge into Baileys Bay.
Fig. 2	Oyster sampling stations in the lower James River.
Fig. 3	Seasonal trends in James River oyster residues.
Fig. 4	Oyster depuration rates.
Fig. 5	Length vs. Kepone residues for channel catfish from the James River.
Fig. 6	Seasonal residue patterns in James River croakers and hogchokers.
Fig. 7	Kepone residue patterns in Chesapeake Bay fishes, 21 June 1976.
Fig. 8	Frequency distribution of Kepone residues in Chesapeake Bay bluefish, 21 June 1976.

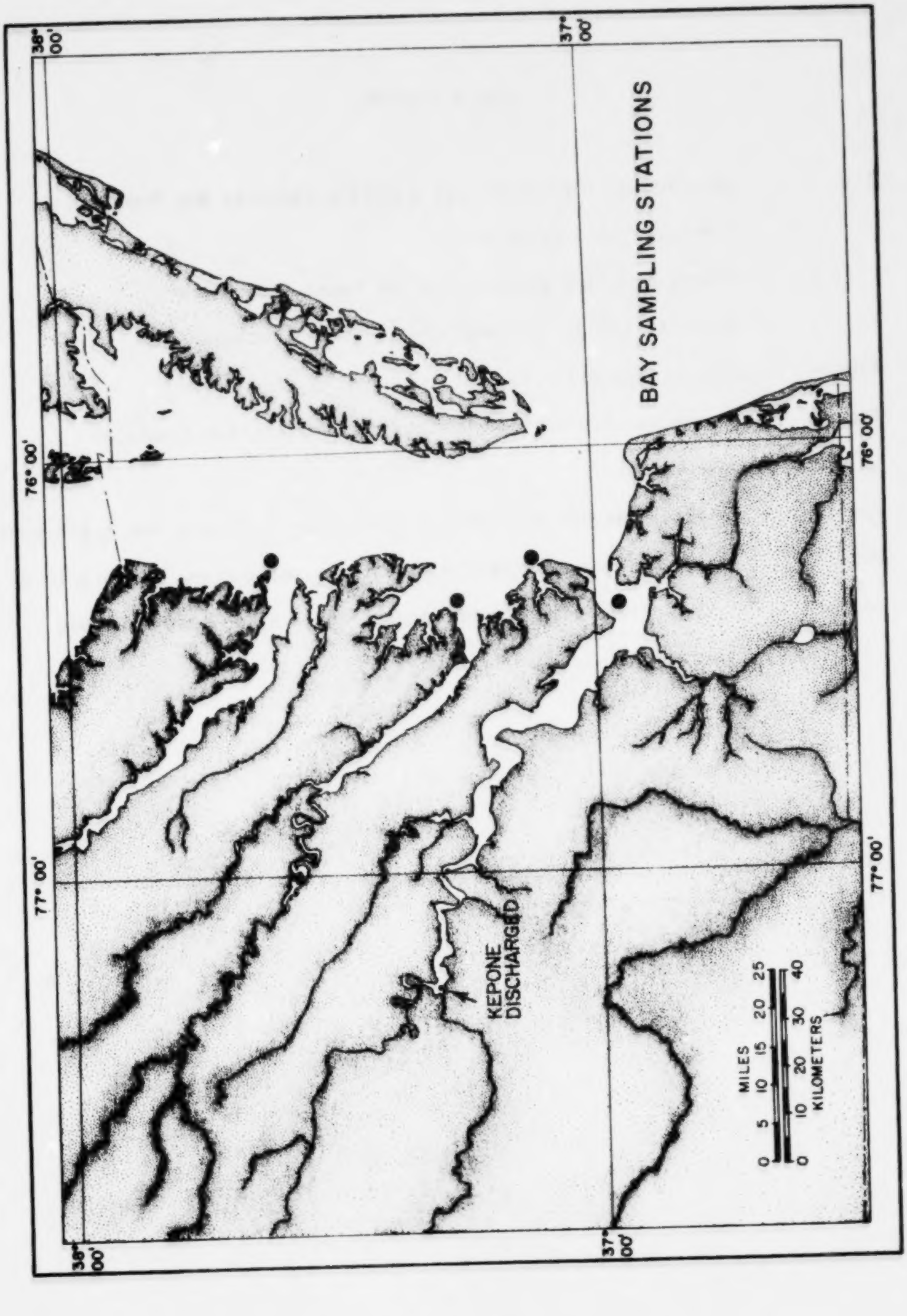
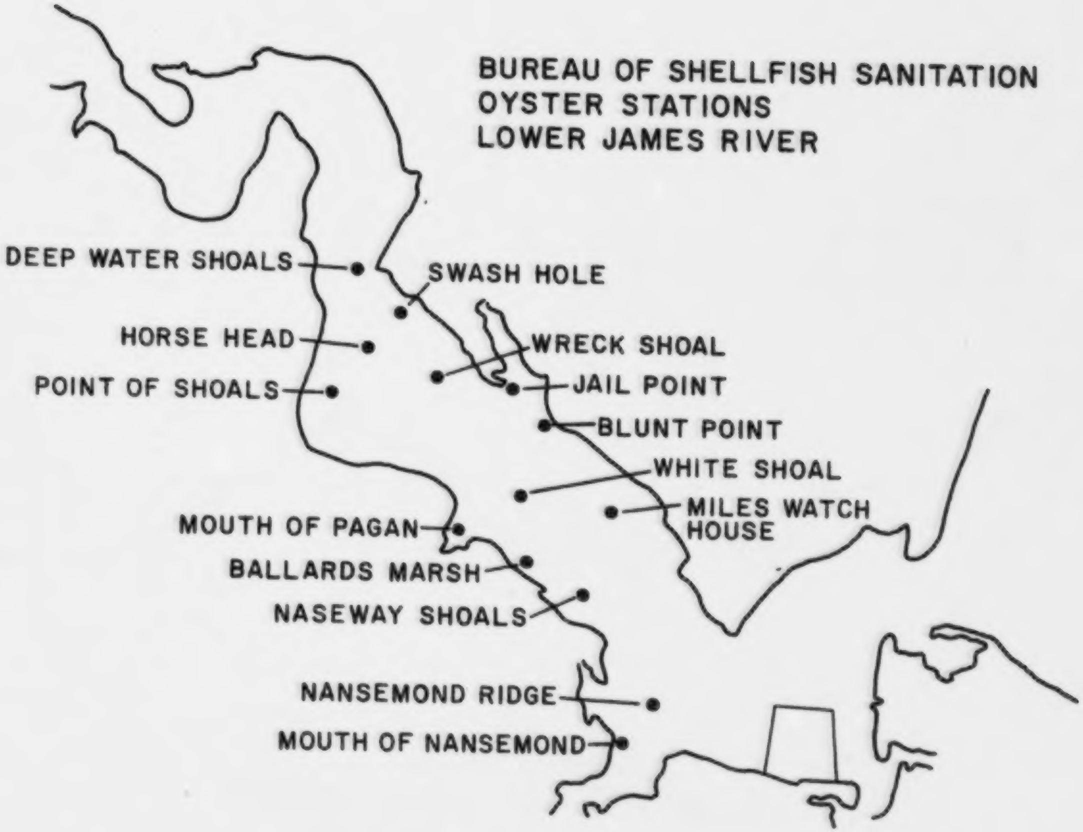

BAY SAMPLING STATIONS
38° 00'
76° 00'
77° 00'
37° 00'
KEPONE DISCHARGED
MILES
0 5 10 15 20 25
0 10 20 30 40
KILOMETERS

FIGURE I



BUREAU OF SHELLFISH SANITATION
OYSTER STATIONS
LOWER JAMES RIVER

DEEP WATER SHOALS
SWASH HOLE
HORSE HEAD
WRECK SHOAL
POINT OF SHOALS
JAIL POINT
BLUNT POINT
WHITE SHOAL
MILES WATCH HOUSE
MOUTH OF PAGAN
BALLARDS MARSH
NASEWAY SHOALS
NANSEMOND RIDGE
MOUTH OF NANSEMOND

FIGURE II

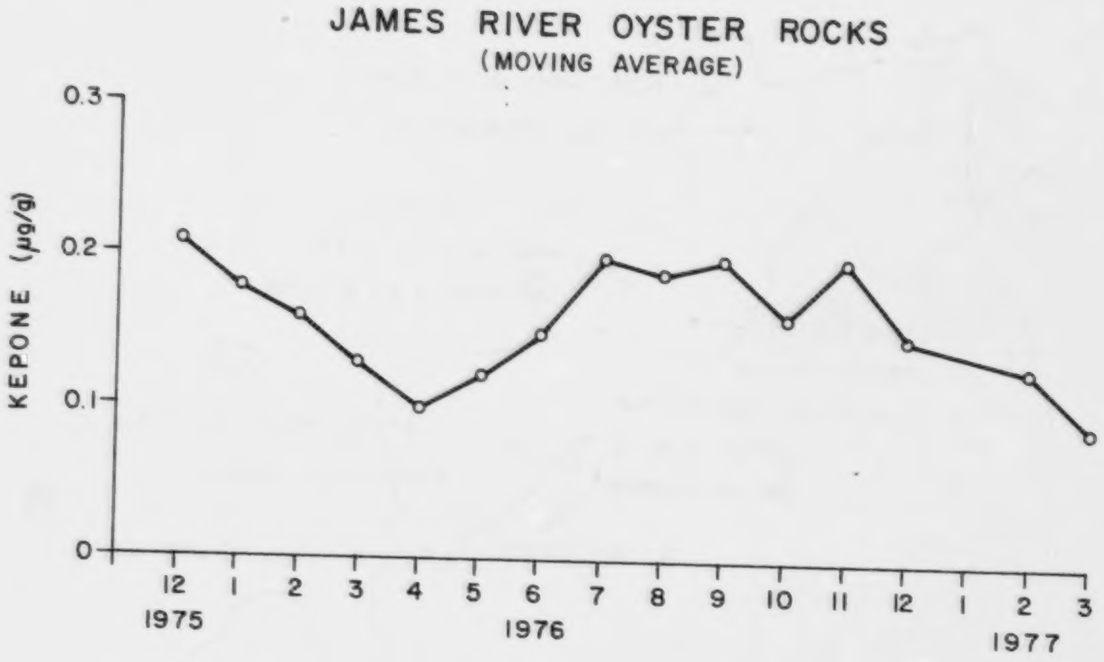

JAMES RIVER OYSTER ROCKS
(MOVING AVERAGE)
KEPONE (μg/g)
0.3
0.2
0.1
0
12
1
2
3
4
5
6
7
8
9
10
11
12
1
2
3
1975
1976
1977

FIGURE III

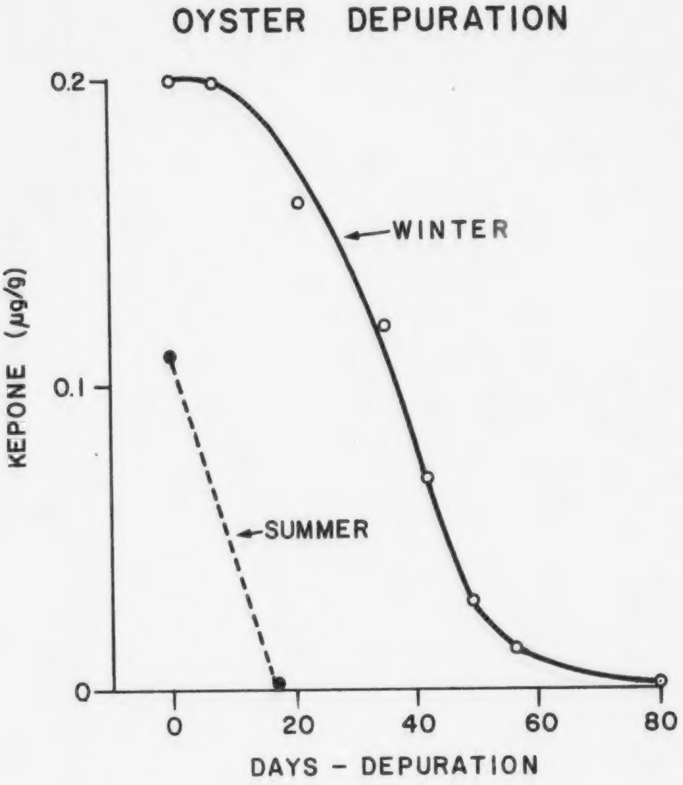

OYSTER DEPURATION
KEPONE (μg/g)
0.2
0.1
0
WINTER
SUMMER
0
20
40
60
80
DAYS - DEPURATION

FIGURE IV

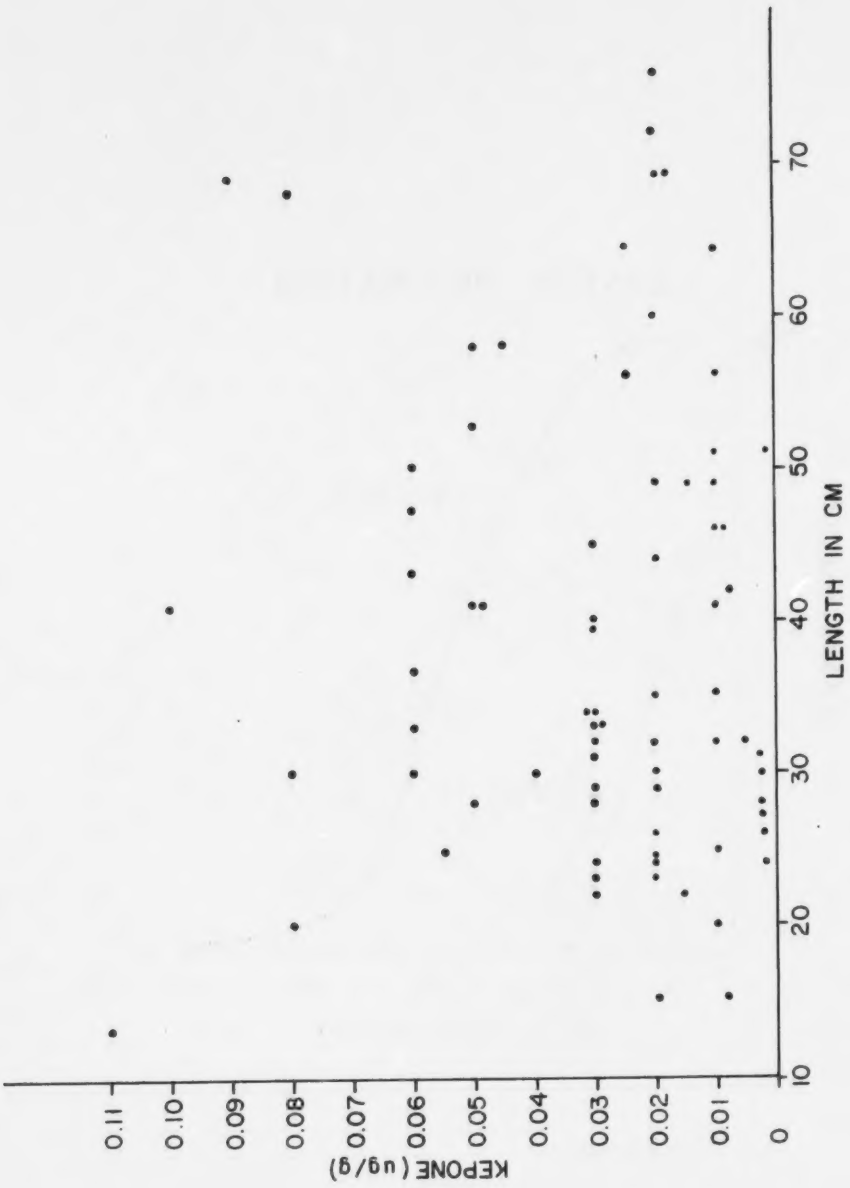

KEPONE (ug/g)
0.11
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
LENGTH IN CM
10
20
30
40
50
60
70

FIGURE V

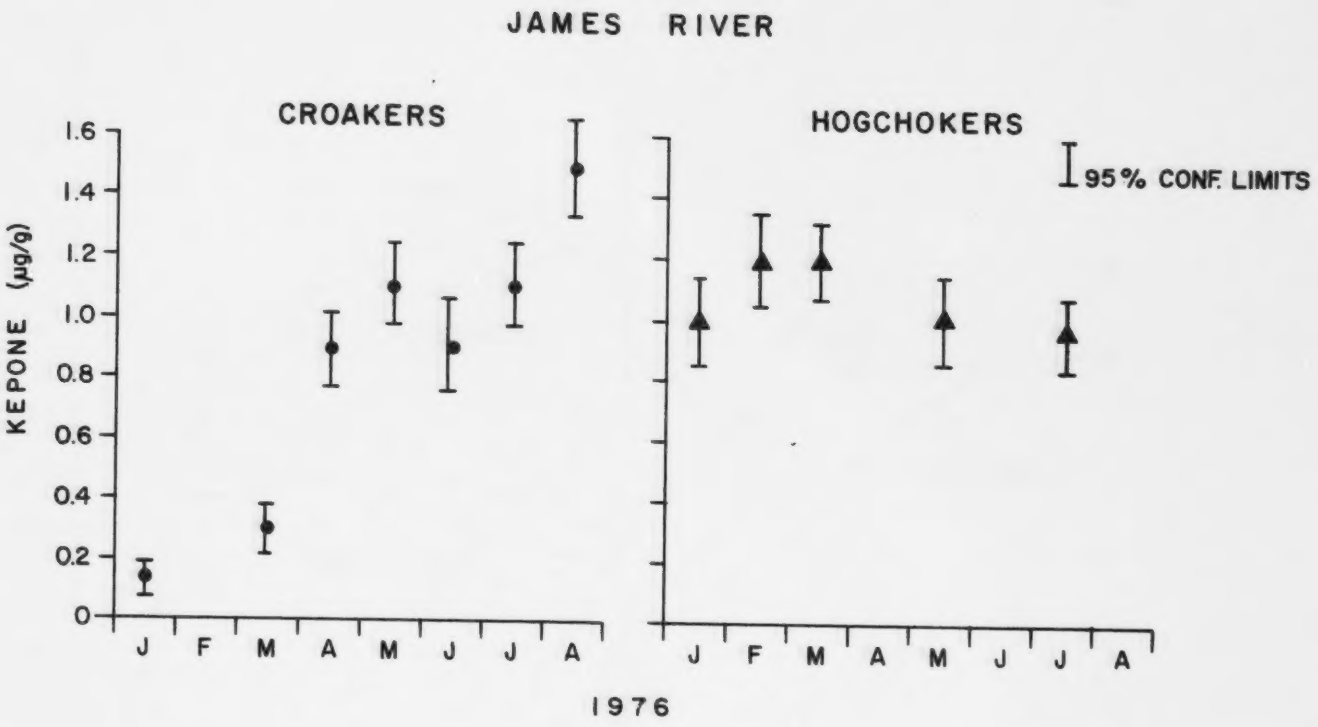

JAMES RIVER
CROAKERS
HOGCHOKERS
95% CONF. LIMITS
KEPONE (µg/g)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
J
F
M
A
M
J
J
A
J
F
M
A
M
J
J
A
1976

FIGURE VI

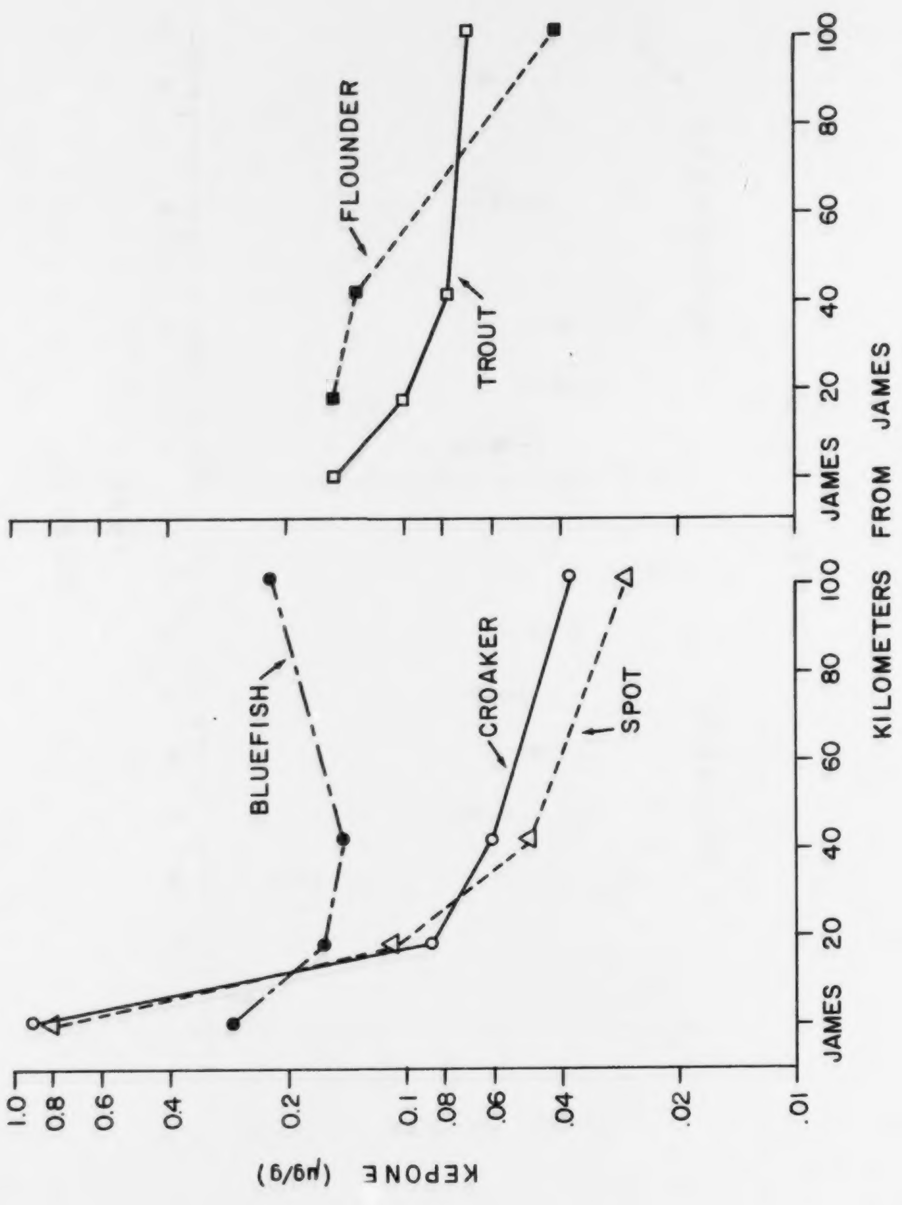

KEPONE (µg/g)
1.0
0.8
0.6
0.4
0.2
0.1
.08
.06
.04
.02
.01
JAMES
20
40
60
80
100
KILOMETERS FROM JAMES
BLUEFISH
CROAKER
SPOT
FLOUNDER
TROUT

FIGURE VII

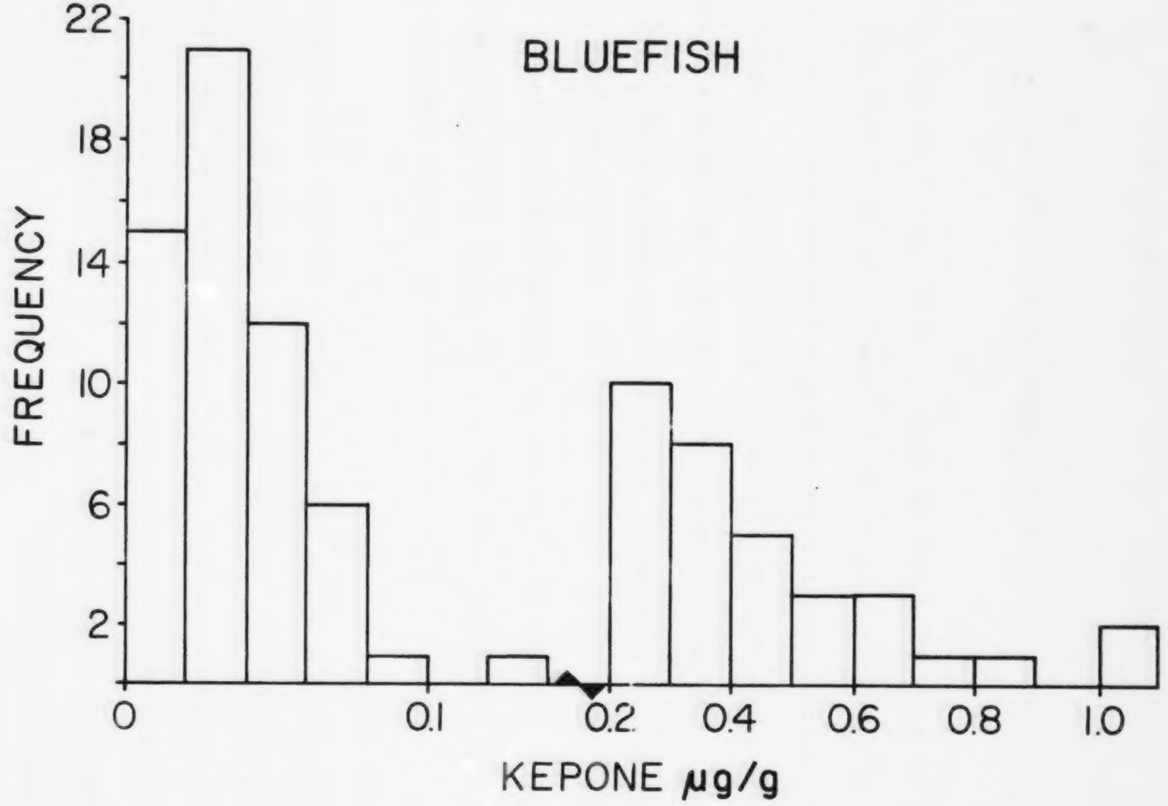


FIGURE VIII

"Current Status of Kepone Problem in Maryland"

Donald H. Noren

Chairman, Maryland Kepone Task Force

and

Director, Maryland Environmental Health Administration

Ladies and gentlemen, good morning. I am pleased to be here and to share with you the current status of the kepone problem in Maryland.

When it became apparent to us in Maryland in February of last year that there was a potential problem in the Baltimore area as a result of kepone stored at the Allied Chemical Plant there, even though the operation was mainly a blending process of kepone that was manufactured at Hopewell, Virginia, Maryland's Health and Mental Hygiene Secretary, Dr. Neil Solomon, formed a Task Force made up of members of various State and Federal agencies which might have some input into defining the extent of any problem that might be existing in Maryland. The Task Force narrowed its concentration to three main areas of concern:

The first was the Allied Plant itself, and the fact that it was right in the way of Interstate 95, which was about to go through the property. The Plant would have to be demolished and most of it decontaminated. The second concern dealt with any health effects from kepone exposure to Allied employees or people living in the vicinity of the plant. The third was the Chesapeake Bay and the marine life it supports.

I would like to bring you up to date on what has transpired as far as the Maryland situation is concerned, because you probably haven't heard too much about it. Let us begin with the Human Health Effects Subcommittee activities. There were approximately 25 to 35 Allied employees in the kepone operation in Maryland. Blood levels were run on the employees both in September 1975 as well as in February 1976. Although none of the employees showed any of the symptoms which the employees in Virginia allegedly evinced, serum kepone levels that were found in Maryland employees were lower than any of those of the Virginia non-cases, that is, those not showing the dramatic symptoms of complainants at Hopewell. The mean level was approximately 500 ppb the first time and approximately 230 ppb the second time samples were analyzed.

Also, the Subcommittee was concerned about a number of residents in the area around the Allied Plant in Baltimore. The Health Department sent out a van in which to screen the individuals by physical examination as well as to draw blood. At the same time, it set up a control group in another part of the city in case additional data were necessary. About 50 percent of the residents appeared for examination; blood was drawn, but no detectable levels of kepone were found in any of these people.

Moreover, there is a playing field of approximately 10 to 11 acres adjacent to the Allied Plant where small amounts of kepone were found in the soil. The park was closed by Order and some of the people who frequented it often, such as coaches and park attendants, were also sampled with no detectable kepone being found in their blood. Also, since the park was closed by Order, one of the priorities of the Task Force was to try to get it reopened. Levels of kepone found in the soil were between two and ten ppm. Ten ppm were found in one or two hot spots. After surveying the park, the portion of land along the Allied property fence was stripped and resodded at Allied's expense, and the park reopened. Additionally, air samples in the vicinity of the plant proved to be negative.

And so the Human Health Effects Subcommittee, while still in existence, has exhausted its immediate responsibility.

The Marine Life Subcommittee was primarily concerned with marine life in Maryland's portion of the Chesapeake Bay estuary, marine life which, because of migratory patterns, might contain kepone ingested in the James River and continuous waters.

The first thing we considered was the prime seed oyster area. A large number of seed oysters which go into private bars in Maryland come from the James River or other Virginia bodies of water. We found that there were approximately 30 to 35 private bars that received shipments of seed oysters from the James River in late 1975 and early 1976. We went to everyone of these private bars, most of which are located around the Annapolis area, in the Severn, West and South rivers, and we sampled everyone of them. Varying degrees of kepone levels were found in the seed oysters, some very low, others non-detectable, but only one was found to be above the FDA action level of 0.3 ppm. That bar was closed off for at least a year, at which time we were to go back and take another look at it. It was sampled again about three weeks later; the level was slightly lower, but again, keep in mind that this was winter time and the depuration rate was slow. I might add that the one lot which showed the highest level was one of the last received from the James River, some time around December or January. We are now awaiting results of samples taken a few days ago from this bar. We further insisted that all seed oysters brought from Virginia waters be certified by Virginia as meeting FDA action levels. At the same time, we also randomly sampled from other natural bars around our portion of the Bay and all samples were below or at the limits of detection.

The next thing we began to look at was crabs. We began sampling the main crabbing areas, again keeping in mind that this was winter time and the crabs weren't moving. Everyone of the crab samples was dug out of the sand, so we had a fairly good indication of location. We started first at the Maryland-Virginia line, Tangier Sound, up the Big and Little Annamessex, up the Nanticoke, the Choptank, Eastern Bay and into the Chester River. We then crossed over to the Patapsco down to the Severn, Patuxent and then the Potomac. The levels that were found in crabs were routinely running below 0.1 ppm, keeping in mind the action level of crabs had been established at 0.4 ppm. None of the samples came near the action level, but the highest levels we did find were in the Baltimore Harbor where the Allied Plant is located. We might find some significance in that, because the third area of concern the Task Force has been dealing with is the plant itself and disposal of waste materials there.

As far as finfish are concerned, we could not sample in February, March or April because the migrations don't begin in Maryland waters usually until May. It was in July, especially, that our finfish monitoring program really went into high gear. The levels of kepone in bluefish that we found then and what we are finding now haven't changed very much. Most of them are running in the .03 to .06 ppm range and these are both on composite as well as individual fish samples.

While we concentrated mostly on bluefish, because they are good indicators, other species, especially rock, are important commercially in Maryland. The levels in rock were not very much different than the levels found in bluefish. Again, slightly lower, but not significantly lower, .02 to .03 pp.

The monitoring program for marine life continues, and the levels, which have been running at approximately .02 ppm or less.

The third area of concern faced by the Task Force was given to a Disposal Subcommittee, and it is this committee which is still wrestling with the Force's most difficult problem. This involves the ultimate disposal of approximately 934 55-gallon steel drums containing pure kepone, technical grade kepone as well as drums of waste and sludge. The problem is compounded because Interstate 95 will go right through the plant site.

In addition, there is an area which had been used as a dump for 70 or more years. It contains anything from rubble debris to clean-out waste and equipment sludge. We found from core samples everything that Allied ever manufactured -- pesticides, heavy metals and other chemicals. Ground water and ecological studies seem to reveal no appreciable movement of ground water in the area, but because a considerable amount of pile-driving and footings will be required for I-95, a temporary cover-seal was placed over the whole dump area to assure that no run-off would take place. A permanent seal will be placed over the area after the highway is completed.

Because of the intrusion of I-95, Allied sold the property to Baltimore City, and has vacated the premises. Before they were permitted to surrender the property, however, the Subcommittee directed Allied, under Subcommittee supervision, to dismantle and decontaminate all machinery and buildings used in the formulation of kepone. It was even necessary to withdraw certain items of machinery from public sale because it appeared there was a remaining contamination problem with some items. Some of the non-saleable metal equipment was incinerated at Bethlehem Steel's Baltimore works.

The remaining problem is now disposal of the drums of kepone and wastes. They had been kept in a quonset hut on the premises, and the vulnerability of the building to vandalism or industrial accident caused no little worry to Task Force members.

Because ultimate disposal and even interim storage pose problems which require some time to solve, the Subcommittee directed Allied to increase security around the quonset hut by erecting 8 feet of chain link fence around the structure, surmounted by 6 feet of barbed wire, by installing an electronic alarm system on all windows and doors, by providing bright night-time lighting and a 24-hour guard.

While incineration of the pure kepone and technical grade material appears to be a viable future ultimate disposal, these only amount to a couple of hundred drums out of the total 934. The remaining material would be difficult to incinerate because there is arsenic present in the stored wastes.

We are now in the process of considering alternative interim storage sites so that all of this material may be removed as I-95 progresses. Some of these alternatives include storage at the Department of the Army's Aberdeen Proving Ground, or storage at other Allied Chemical facilities.

While an environmental assessment of storage at Aberdeen, commissioned by Allied Chemical, has reported no environmental danger would occur if that site were selected, and the Kepone Task Force has recommended to Secretary Solomon that the assessment be accepted as technically sound, we are awaiting Allied Chemical's formal application to the Department of the Army for permission to use the Aberdeen facility for such interim storage. We can only wait and see what decision will ultimately be reached, but at this time, it would appear that this is by far the most practical and the safest manner to isolate this material until final disposal methods are ultimately developed. Thank you.

The Current Efforts of Virginia Agencies to Monitor Kepone in the Environment

Michael A. Bellanca

William F. Gilley

INTRODUCTION

The EPA Health Effects Research Laboratory released its preliminary report in December 1975 on environmental Kepone levels found in fish, water, sediment and shellfish in the James River system. From this indication of the extensiveness of Kepone contamination in environment, the Virginia Kepone Task Force directed the establishment of a comprehensive Monitoring Program with responsibilities divided between the State Water Control Board, State Department of Health and the Virginia Institute of Marine Sciences. The 1976 monitoring effort focused on drinking water, surface water, groundwater, sediment, non-point source studies, finfish, shellfish, and crab. Currently, the monitoring program includes finfish, crab, shellfish, sediment and water at approximately 60 locations in the James River and Chesapeake Bay.

The primary purpose of the monitoring and surveillance effort was to verify environmental levels and trends in assessing the magnitude of the contamination. It was designed to provide a data base from which actions could evolve for protection of the public health. With the accumulation of data, the James River remains restricted to taking of finfish and crabs. The same effort has supported the early finding that Kepone was principally confined to the River with finfish levels in the Bay continuing well below the current action level.

With the containment of Kepone in the Hopewell area, an added purpose of surveillance is to verify integrity of control or determine losses to the environment. In developing plans for future actions, the priorities for clean-up can only be established with such data derived from the broadly based monitoring effort.

As Dr. Bender has already discussed the levels of Kepone found in the biota, this discussion of the monitoring program will concentrate on sediment and water sampling as well as set forth the finfish and crab sampling effort of the State Water Control Board and Bureau of Shellfish Sanitation of the Department of Health.

SEDIMENT MONITORING

The source and extent of Kepone contamination in the James River and its tributaries has been traced and is monitored now by sediment sampling. In the sediment, Kepone may be stored in one of two compartments. It may exist in solution within the interstitial water of the sediments or may be absorbed to sediment particles. Moreover, Kepone may become incorporated into the organic portion of the sediments either in living organisms or in the remains of dead ones, or it may be associated with petroleum hydrocarbons absorbed to sediment material. The relative abundance of Kepone in each of these compartments is a function of the following factors: sediment size and composition, and the depth within the sediments; temperature and pH (which invluence Kepone solubility, volatility, and sorption-desorption reactions); and the amount of organic matter present. The transfer of Kepone from the sediments to the water column could occur through resuspension of sediment solids, desorption from sediment solids, and dispersal of the soluble portion originally contained in the sediment interstitial water.

While the primary purpose of 1976 Kepone sediment monitoring was to determine the location and depth of Kepone in river sediments, it was believed that this knowledge along with an understanding of the mechanisms of sediment transport below Hopewell, Virginia, would help determine the mobility of the Kepone reservoir in the James River. In addition this data, when incorporated into sediment concentration map, would be useful in evaluating the feasibility of proposals to remove or control the Kepone-contaminated sediments (e.g. estimation of the amount of material which would have to be dredged and ultimately disposed on land). Moreover, this data would provide valuable information regarding the potential hazard of dredging in specific areas (e.g. Kepone uptake by fish and shellfish).

SEDIMENT MONITORING STATIONS

From January to May 1976, Division of Ecological Studies personnel collected sediment core samples at 51 stations in the James River estuary and its tributaries (Figure 1). The 51 stations and sediment cores are briefly described in Table 1. Using a Phleger gravity corer, six cores were collected at each station. Each was labelled according to station and substrate characteristics. Core samples were frozen using dry ice and transported to the laboratory for sectioning. In submitting the sediment samples, the top half inch was removed from five of six cores and composited. Below the top half inch, one-inch increments of sediment were removed and similarly prepared. The sixth core sample from each station was kept for future reference. Sediment samples were submitted to the Division of Consolidated Laboratory Services (DCLS), Richmond, Virginia for Kepone analysis.

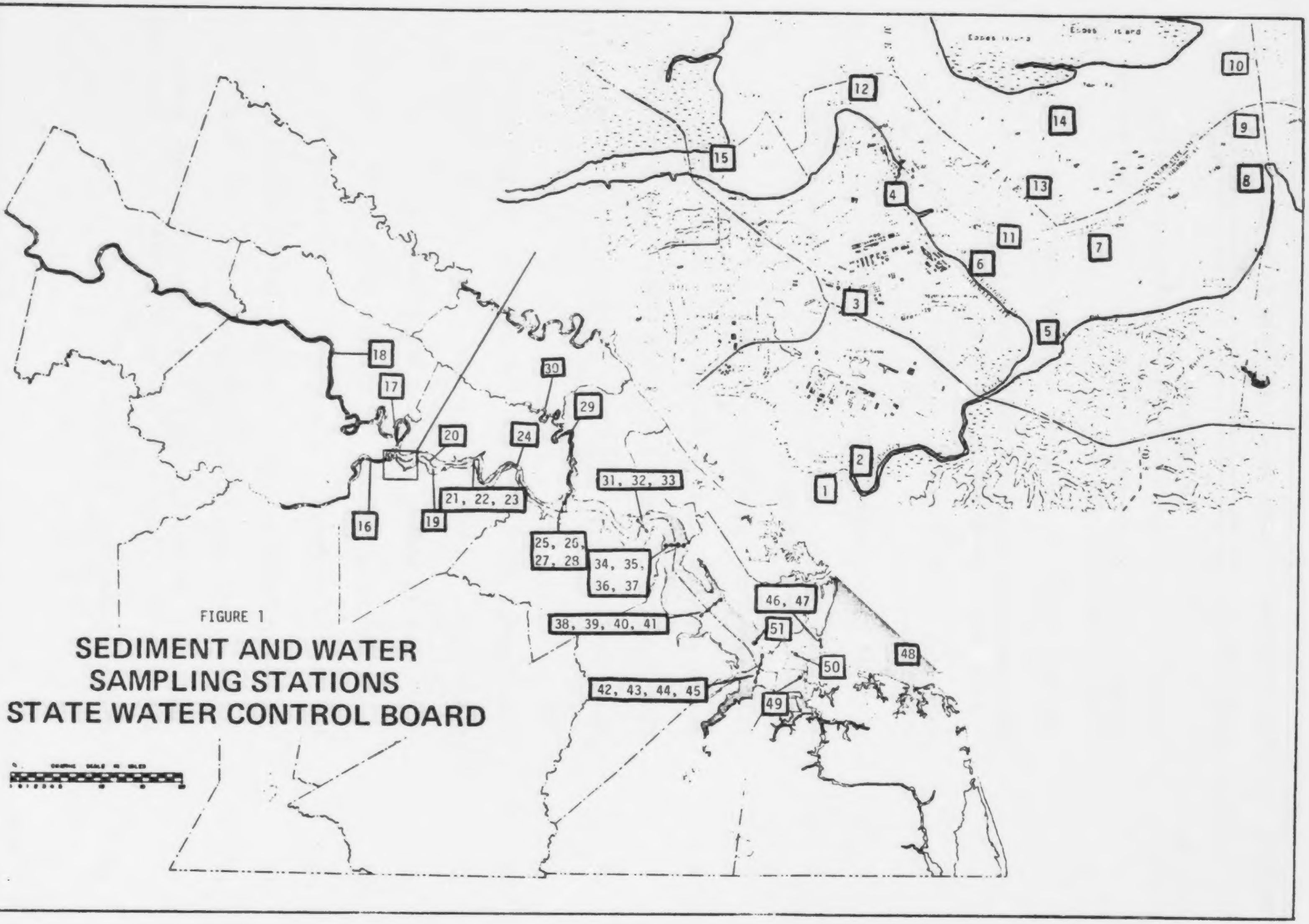

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FIGURE 1

SEDIMENT AND WATER
SAMPLING STATIONS
STATE WATER CONTROL BOARD

TABLE 1. Brief Description of Stations and Sediment Cores.

STATION	DESCRIPTION
1	Hopewell STP, swampy area between the effluent and Bailey Creek. Highly organic mud.
2	Landfill beside Hopewell STP. Organic mud with some sand.
3	The upstream portion of Gravelly Run draining with Pebble A & N plant. Sandy sediment with some organic mud.
4	Poythriss Creek at confluence of Bailey Bay. Highly organic mud.
5	Mouth of Bailey Creek. Highly organic mud.
6	Bailey Bay, in front of Continental Can complex. Organic mud with woody material.
7	Mid-Bailey Bay. Highly organic mud.
8	Bailey Bay area, west of Jordan Point. Highly organic mud.
9	Mid-channel at Benjamin Harrison Bridge. Brown mud.
10	North shore of James River near Harrison Point. Upper portion of core (0 - 0.5") light silt; (0.5 - 3.5") brown mud.
11	Mid-channel, off Continental Can complex. Sandy sediment.
12	Mid-channel, off City Point. Brown mud.
13	Spoil area in middle of Bailey Bay. Brown mud.
14	Bailey Bay area, 850 yds. NE of station 13. Dark brown mud.
15	Mid-channel at Buzzard Island, mouth of Appomattox River.
16	Appomattox River at Point of Rocks. Sandy sediment.
17	Turkey Island cutoff, in the channel. Gray-brown mud.
18	James at Deepwater Terminal, in the channel. Upper portion of core (0 - 0.5") light silt and leaves; (0.5 - 3.5") sandy sediment.
19	Middle of Tar Bay. Brown mud.

TABLE 1. Continued.

STATION	DESCRIPTION
20	Tar Bay area, mid-channel at buoys C99 and R100.
21	Windmill Point spoil area. Brown mud.
22	James River at Buoy C85. Dark brown mud.
23	Windmill Point, north shore. Sandy brown mud.
24	James River, channel at Kennon Marsh. Brown mud.
25	Mouth of Chickahominy River at buoy R68. Gray organic mud.
26	Mouth of Chickahominy, north of buoy R68. Brown mud.
27	Mouth of Chickahominy, off Barrets Point. Gray mud.
28	Mouth of Chickahominy, channel at buoy R6A. Gray sandy mud.
29	Chickahominy River, channel at buoy R10. Dark brown mud with shells.
30	Chickahominy River below Walkers Dam. Black mud.
31	James River, west side of Hog Island. Brown mud.
32	James River, west side of Hog Island. Brown mud.
33.	James River, west side of Hog Island. Dark brown mud.
34	Deepwater shoals transect. Dark brown mud.
35	Deepwater shoals transect. Brown mud.
36	Deepwater shoals transect. Brown mud.
37.	Deepwater shoals transect. Sandy brown mud.
38	Blunt Point transect.through J11. Dark brown mud.
39	Blunt Point transect through J11. Brown mud.
40	Blunt Point transect through J11. Brown-gray mud.
41	Blunt Point transect through J11. Gray-sandy mud with shells.

TABLE 1. Continued.

STATION	DESCRIPTION
42	Newport News Transect, BW H11 to Pig Point. Brown mud.
43	Newport News Transect, BW H11 to Pig Point. Dark Brown Mud.
44	Newport News Transect, BW H11 to Pig Point. Dark Brown mud.
45	Newport News Transect, BW H11 to Pig Point. Brown-gray sandy mud.
46	James River, Hampton Roads bridge tunnel. Sandy dark brown mud.
47	James River, Hampton Roads bridge tunnel. Dark brown mud.
48	Chesapeake Bay, buoy R10. Thimble Shoals channel. Dark brown mud.
49	Norfolk Harbor reach, midway between buoys R12 and R14. Black mud.
50.	Newport News channel, between buoys 7 and 8. Sandy gray mud.
51	Off Newport News Shipbuilding and Drydock. Sandy gray mud.

RESULTS OF SEDIMENT ANALYSIS

The results of Kepone analyses of 235 samples from 51 stations are presented in Table 2. Kepone values are in parts per million (ppm). An attempt was made to submit successively deeper samples until non-detected levels were reached in two adjacent increments for a given station. This has been achieved for most stations.

Using the following ranges, Kepone distribution maps (Figures 2, 3, and 4) were produced representing average levels in the top 3.5 inches of sediment; greater than 10.0 ppm, very heavy contamination; 1.0 to 9.99 ppm, heavy contamination; 0.1 to 0.99 ppm, trace contamination; and no Kepone detected at detection levels of 0.01 to 0.02 ppm. Table 3 represents a breakdown of stations 1-51 into these ranges.

It appears that only the sediments in Bailey Bay, Bailey Creek below the Hopewell STP and certain small tributaries to Bailey Creek are heavily contaminated (Stations 1, 3, 5, and 8). The James River above the Turkey Island cut-off and the Appomattox River appears to be uncontaminated, at least in the channels (Stations 15 to 18). Other areas in Bailey Creek, Bailey Bay and Tar Bay with moderate contamination included stations 2, 4, 6, 7, 13, 19, and 20 (Figure 2). Channel areas within Bailey Bay show non-detected (Station 9 and 11) to trace levels (Station 12) of Kepone. These sediments are subject to scouring and periodic dredging, preventing organic fine-grained material from settling. Stateions off Harrison Point (Station 10) and Eppes Island (Station 14) showed non-detected to trace levels, respectively. The non-detected level at Station 10 is somewhat suspect. Cores collected at this Station on January 13, 1976 were characterized as brown silt and clay. In a separate study conducted on March 23, 1977, twelve cores were collected at four stations in close proximity to Station 10, and Kepone level of 0.12 ppm was found in a composite sample of the top six inches. These cores were primarily composed of brown-gray silt and clay. While the difference in levels may be due to variations in space and time, results of the latter study, where more cores were collected over a larger area, seem to indicate that trace to moderate levels of Kepone probably occur on this north shore area of the James River.

At stations downstream of Tar Bay past the confluence of the James and Chickahominy Rivers (Stations 21 to 24, 27, and 28), there appears to be trace to moderate (Stations 25 and 26) contamination (Figures 3 and 4). At this confluence the James becomes wider and shallower, and this area may be an important settling-out region for fine Kepone-laden sediments. Chickahominy River Stations 29 and 30 show that trace levels may have been deposited upstream as far as Walkers Dam, possibly by aerial dispersion.

Twenty stations (31 to 51) were sampled between the Chickahominy confluence and Hampton Roads. Of these, only Station 32, 34, 35 and 39 had moderate Kepone levels in the top 3.5 inches. Station 39, in the channel

TABLE 2. Results of Kepone Analysis of James River Basin Sediment Core Samples Collected in 1976. Kepone values in ppm.

Depth		Station Number											
Inches	Cm	1	2	3	4	5	6	7	8	9	10	11	12
0.0-0.5	0.0-1.27	26.80	0.28	3.4	0.46	5.2	1.8	0.11	5.1	ND*	ND*	ND*	0.058
0.5-1.5	1.27-3.81	23.80	0.41	1.1	0.15	1.3	0.13	0.22	3.4	ND*	ND*	ND*	ND*
1.5-2.5	3.87-6.35	0.51	0.087	1.86	0.16	1.7	0.52	0.23	2.9				ND*
2.5-3.5	6.35-8.89	0.11	0.41	0.29	0.15	1.0	0.71	0.068	2.1				ND*
3.5-4.5	8.89-11.43				0.39	0.35	0.42	0.034	1.3				
4.5-5.5	11.43-13.97				ND*	2.9	1.18	0.07	1.2				
5.5-6.5	13.97-16.51				ND*	1.12	0.36	0.01	0.95				
6.5-7.5	16.57-19.05					ND*		ND*	ND*				
7.5-8.5	19.08-21.59					ND*			ND*				
8.5-9.5	21.59-24.13												
9.5-10.5	24.13-26.67												
10.5-11.5	26.67-29.21												
11.5-12.5	29.21-31.75												
12.5-13.5	31.75-34.29												
13.5-14.5	34.29-36.83												
14.5-15.5	36.83-39.37												

ND* - None detected at 0.02 ppm level of detection.
ND**- None detected at 0.01 ppm level of detection.

TABLE 2. Continued.

Depth		Station Number										
Inches	Cm	13	14	15	16	17	18	19	20	21	22	23
0.0-0.5	0.0-1.27	0.020	0.006	ND**	ND**	ND**	ND*	0.11	0.099	0.025	0.031	0.017
0.5-1.5	1.27-3.81	0.030	0.002	ND**	ND**	ND**	ND*	0.08	0.13	0.22	0.013	0.054
1.5-2.5	3.87-6.35	0.19	0.07					0.26	ND*	0.11	0.12	ND*
2.5-3.5	6.35-8.89	0.17	0.06					0.86	0.35	0.03	0.12	ND*
3.5-4.5	8.89-11.43	0.02	0.07					0.02	0.19	0.10	0.01	
4.5-5.5	11.43-13.97	0.10	0.12					0.16	0.06	0.13	0.36	
5.5-6.5	13.97-16.51	0.17	ND*					0.09	0.02	0.08	ND*	
6.5-7.5	16.57-19.05	ND*	ND*					ND*	0.03	0.12	ND*	
7.5-8.5	19.08-21.59	ND*							0.13	0.14		
8.5-9.5	21.59-24.13											
9.5-10.5	24.13-26.67											
10.5-11.5	26.67-29.21											
11.5-12.5	29.21-31.75											
12.5-13.5	31.75-34.29											
13.5-14.5	34.29-36.83											
14.5-15.5	36.83-39.37											

ND* - None detected at 0.02 ppm level of detection.

TABLE 2. Continued.

Depth		Station Number											
Inches	Cm	24	25	26	27	28	29	30	31	32	33	34	35
0.0-0.5	0.0-1.27	ND*	0.18	0.15	0.18	0.10	ND*	0.022	0.028	0.16	0.12	0.12	0.09
0.5-1.5	1.27-3.81	0.04	0.49	0.45	0.088	0.090	ND*	0.001	ND**	0.18	0.16	0.58	0.61
1.5-2.5	3.87-6.35	0.10	0.20	0.30	ND*	ND*		0.01	ND**	0.06	ND**	ND*	0.12
2.5-3.5	6.35-8.89		0.20	0.13	ND*	ND*		ND**	ND**	0.10	ND**		0.14
3.5-4.5	8.89-11.43		0.49	0.08						0.11			0.19
4.5-5.5	11.43-13.97		0.15	0.19						0.10			0.14
5.5-6.5	13.97-16.51		0.02	0.12						0.11			0.21
6.5-7.5	16.57-19.05		0.06	0.04						0.12			0.26
7.5-8.5	19.08-21.59		0.22	ND*									
8.5-9.5	21.59-24.13												
9.5-10.5	24.13-26.67												
10.5-11.5	26.67-29.21												
11.5-12.5	29.21-31.75												
12.5-13.5	31.75-34.29												
13.5-14.5	34.29-36.83												
14.5-15.5	36.83-39.37												

*ND - None detected at 0.02 ppm level of detection.
**ND - None detected at 0.01 ppm level of detection.

TABLE 2. Continued.

Depth		Station Number												
Inches	Cm	36	37	38	39	40	41	42	43	44	45	46	47	48
0.0-0.5	0.0-1.27	0.057	ND*	ND*	0.28	0.071	0.047	ND*	0.03	0.032	ND*	ND*	ND*	ND*
0.5-1.5	1.27-3.81	0.17	ND*	ND*	0.77	0.060	ND**	ND*	ND*	0.025	ND*	ND*	ND*	ND*
1.5-2.5	3.87-6.35	ND*			0.24	0.02	ND*		0.03	ND*				
2.5-3.5	6.35-8.89	0.02			ND*	ND*	ND*		ND*	ND*				
3.5-4.5	8.89-11.43				ND**	ND*								
4.5-5.5	11.43-13.97													
5.5-6.5	13.97-16.51													
6.5-7.5	16.57-19.05													
7.5-8.5	19.08-21.59													
8.5-9.5	21.59-24.13													
9.5-10.5	24.13-26.67													
10.5-11.5	26.67-29.21													
11.5-12.5	29.21-31.75													
12.5-13.5	31.75-34.29													
13.5-14.5	34.29-36.83													
14.5-15.5	36.83-39.37													

*ND - None detected at 0.02 ppm level of detection.

**ND- None detected at 0.01 ppm level of detection.

TABLE 2. Continued.

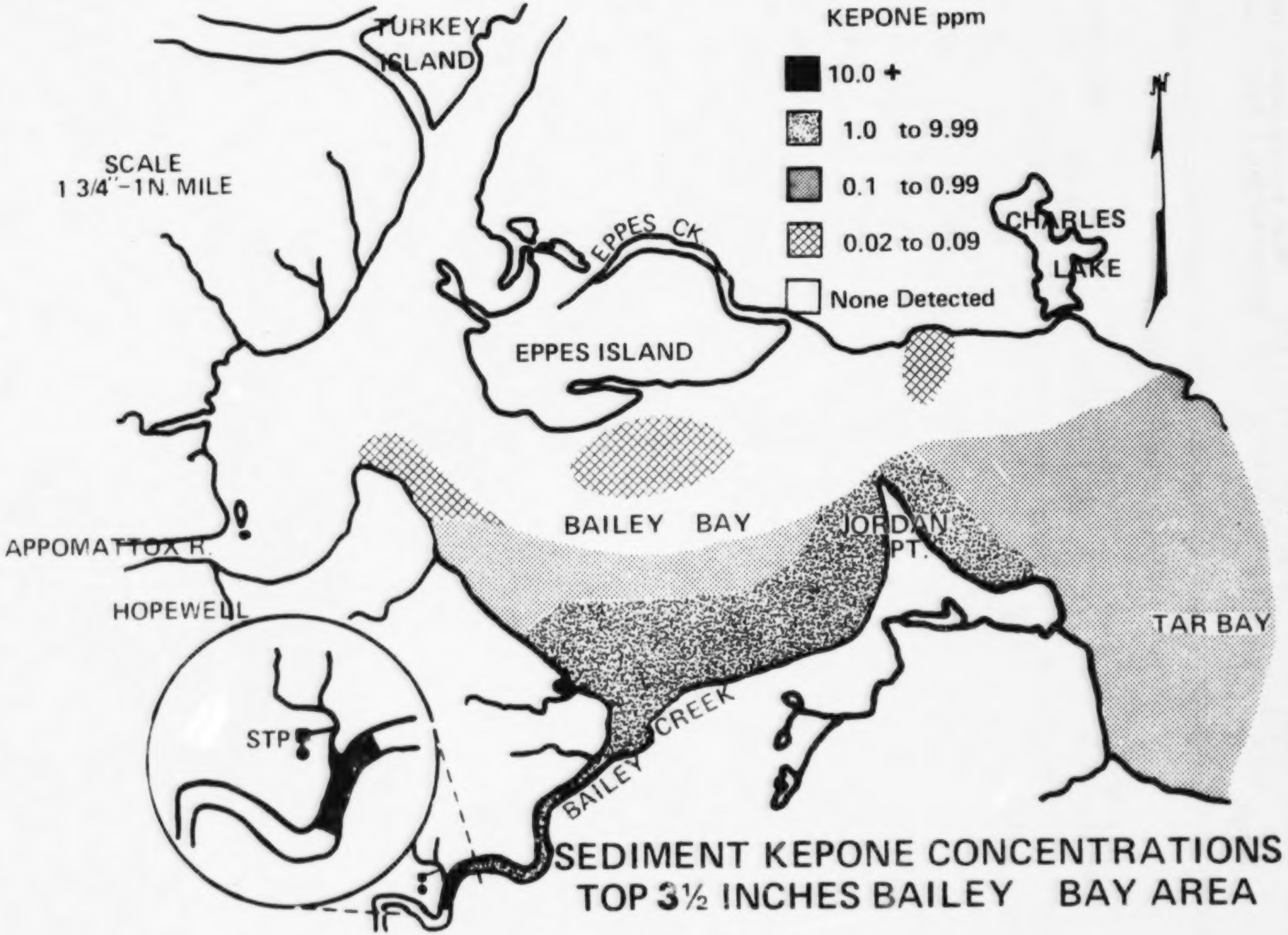
Depth		Station Number		
Inches	Cm	49	50	51
0.0-0.5	0.0-1.27	0.080	ND*	ND*
0.5-1.5	1.27-3.81	0.051	ND*	ND*
1.5-2.5	3.87-6.35	ND*		
2.5-3.5	6.35-8.89	ND*		
3.5-4.5	8.89-11.43			
4.5-5.5	11.43-13.97			
5.5-6.5	13.97-16.51			
6.5-7.5	16.57-19.05			
7.5-8.5	19.08-21.59			
8.5-9.5	21.59-24.13			
9.5-10.5	24.13-26.67			
10.5-11.5	26.67-29.21			
11.5-12.5	29.21-31.75			
12.5-13.5	31.75-34.29			
13.5-14.5	34.29-36.83			
14.5-15.5	36.83-39.37			

*ND - None detected at 0.02 ppm level of detection.
**ND- None detected at 0.01 ppm level of detection.

Table 3. Kepone Contamination Ranges for Stations 1-51. Mean Kepone Levels for the Top 3.5 Inches Were Used to Place Each Station Within a Particular Range.

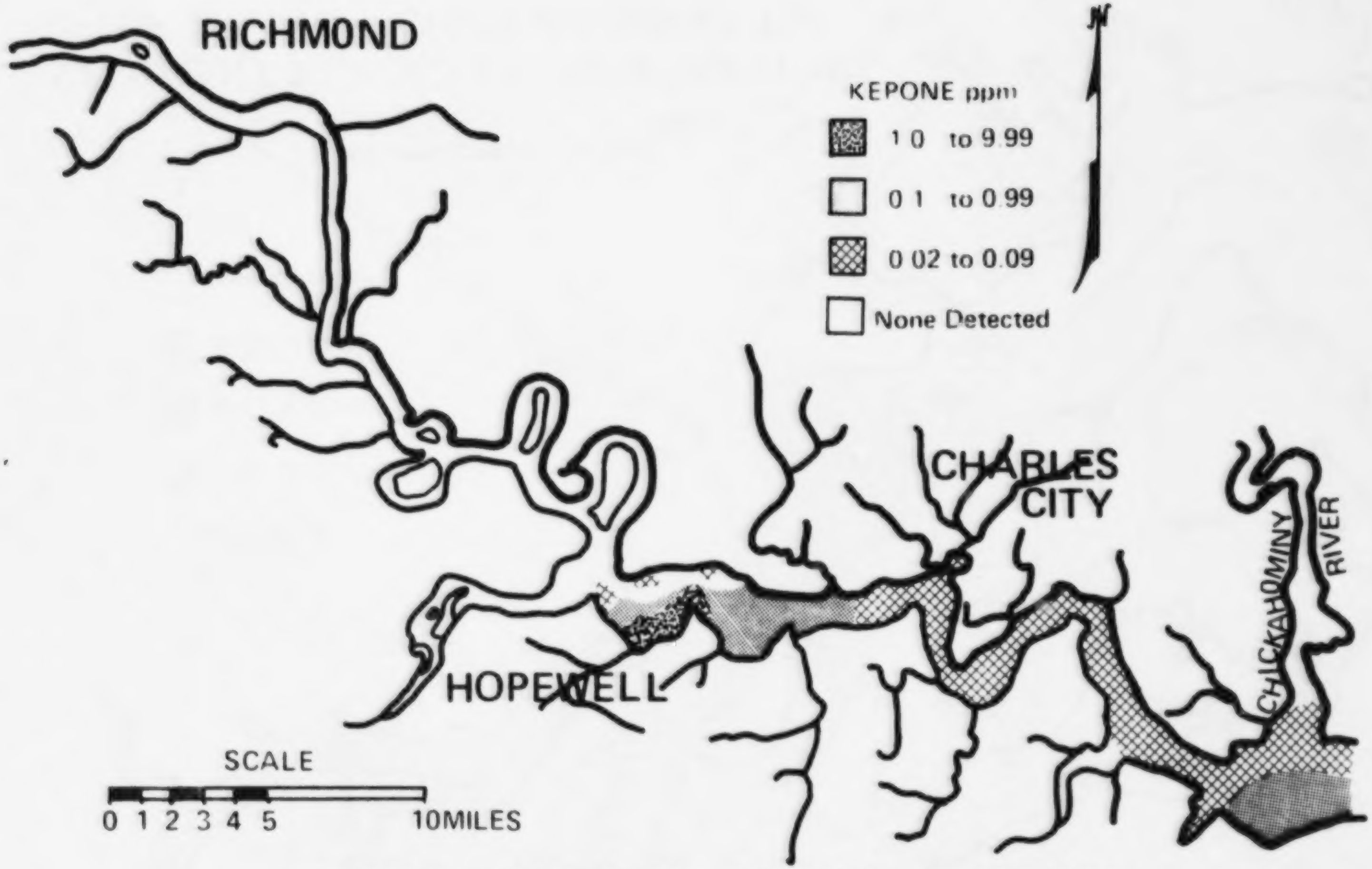
	Kepone Contamination Range (ppm)				
	Very heavy Greater 10.0	Heavy 1.0 to 9.99	Moderate 0.1 to 0.99	Trace 0.02 to 0.09	Non-Detected ND
Station	1	3	2	12	9
		5	4	14	10
		8	6	21	11
			7	22	15
			13	23	16
			19	24	17
			20	27	18
			25	28	29
			26	30	37
			32	31	38
			34	33	42
			35	36	45
			39	40	46
				41	47
				43	48
				44	50
				49	51

FIGURE 2


TURKEY ISLAND
SCALE 1 3/4"–1N. MILE
KEPONE ppm
■ 10.0 +
▨ 1.0 to 9.99
▨ 0.1 to 0.99
▨ 0.02 to 0.09
□ None Detected
N
EPPES CK
CHARLES LAKE
EPPES ISLAND
BAILEY BAY
JORDAN PT.
APPOMATTOX R.
HOPEWELL
TAR BAY
STP
BAILEY CREEK

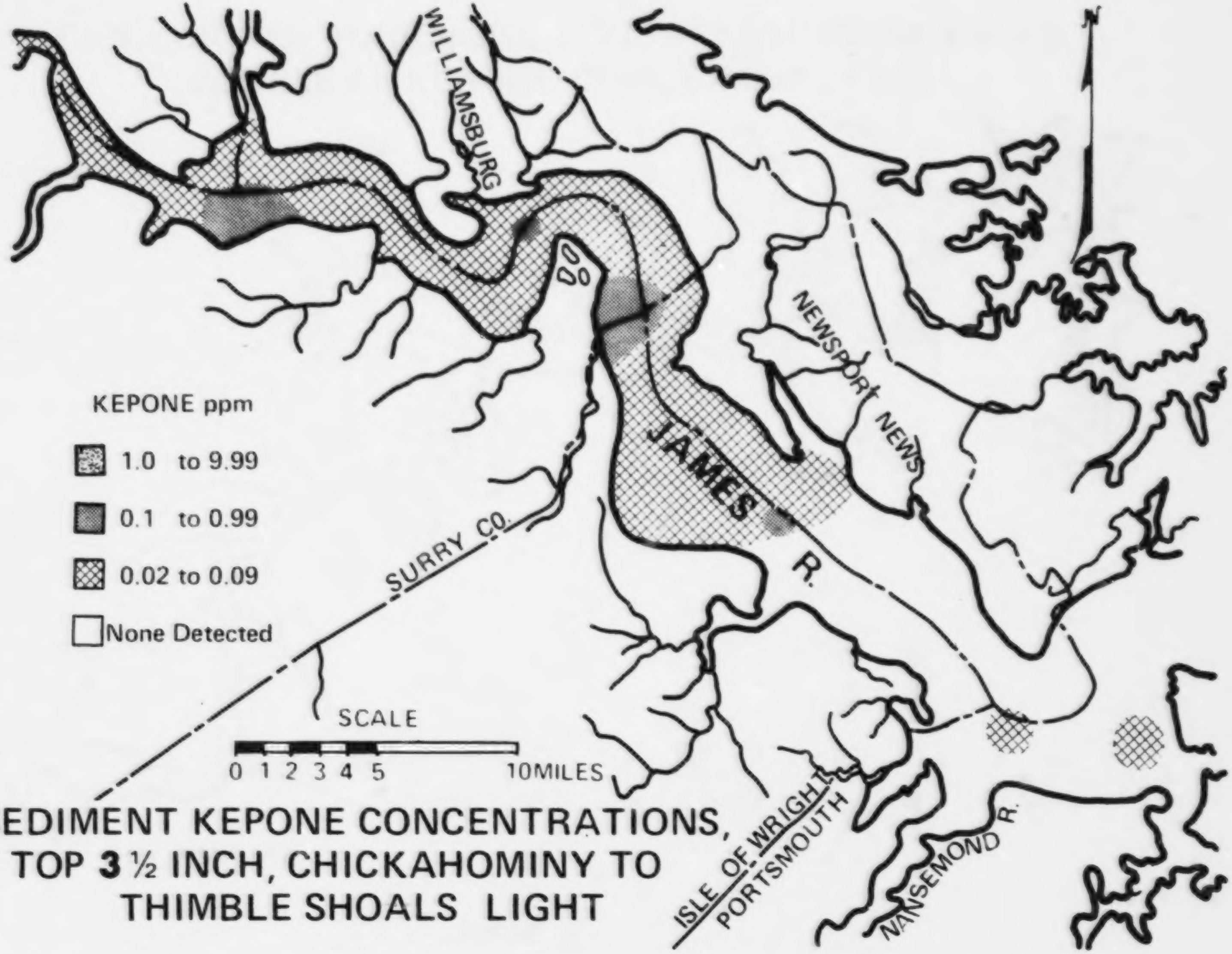
SEDIMENT KEPONE CONCENTRATIONS TOP 3½ INCHES BAILEY BAY AREA

FIGURE 3


RICHMOND
KEPONE ppm
▨ 1.0 to 9.99
☐ 0.1 to 0.99
▨ 0.02 to 0.09
☐ None Detected
N
CHARLES CITY
CHICKAHOMINY RIVER
HOPEWELL
SCALE
0 1 2 3 4 5 10MILES

SEDIMENT KEPONE CONCENTRATIONS
TOP 3½ INCHES, RICHMOND TO CHICKAHOMINY RIVER

FIGURE 4


N
WILLIAMSBURG
NEWSPORT NEWS
JAMES R.
SURRY CO.
ISLE OF WRIGHT
PORTSMOUTH
NANSEMOND R.
KEPONE ppm
▨ 1.0 to 9.99
■ 0.1 to 0.99
▩ 0.02 to 0.09
☐ None Detected
SCALE
0 1 2 3 4 5 10MILES

SEDIMENT KEPONE CONCENTRATIONS, TOP 3 ½ INCH, CHICKAHOMINY TO THIMBLE SHOALS LIGHT of the Blunt Point transect, represents the most distant point downstream below Hopewell where a moderate level (0.33 ppm) of Kepone has been measured. Station 32 located in the Goose Hill Channel west of the Hog Island transect had a Kepone level of 0.13 ppm. Station 34 (mud flat) and 35 (channel) were in the Deep Water Shoals transect and both had a Kepone level of 0.24 ppm. The remaining stations contained trace to non-detected levels of Kepone. Stations 42 to 51 in the Hampton Roads area had trace to non-detected Kepone levels. This information has had some influence on decisions involving dredging projects in the region.

Using the results of these Kepone sediment data, a tentative estimate of the Kepone burden in the River has been approximately 100,000 pounds. This burden then functions as the supply reservoir for continued uptake by finfish and other biota.

FUTURE KEPONE SEDIMENT MONITORING

The proposed Kepone sediment monitoring program for 1977 will include 45 of the 51 previous stations, with only 16 to 18, 37, 50 and 51 being deleted. Station-to-Station and comprehensive comparison of 1976 and 1977 data should help in determining if: (1) Kepone levels in the James River have reached an equilibrium; (2) Kepone levels have decreased across-the-board indicating that the sum of photo degradation, microbial degradation, bioaccumulation and loss by River transport (resuspension) exceeds the net input of Kepone; (3) there appears to be a downstream shift in the Kepone reservoir. There is the distinct possibility that the flux of Kepone within the sediment is influenced by two or more of these factors.

Several modifications have been made from the 1976 Kepone sediment sampling procedure. Thirteen new Kepone stations have been established to determine Kepone levels within areas not previously examined and to allow refinement of Kepone maps. These new stations (52 to 64) produce a total of 58 which will be sampled during 1977.

This year, five cores will be collected at each station. Of these, one will be maintained as a reference core. The other four will be sectioned and composited at the following increments: 0-3.5 inches, 3.5-6.5 inches, 6.5-12.5 inches and 12.5-18.5 inches. Trends in Kepone levels with depth will be examined. In addition, portions of the composited cores will be used for total organic carbon (TOC) and grain size analysis, both of which will be correlated to Kepone levels within each increment. An effort will also be made to analyze Kepone levels within water samples from each station along with a corresponding measurement of suspended particulate matter.

GROUNDWATER

In addition to the estimate of 100,000 pounds of Kepone in the river system, other quantities were disposed of in the city landfill and other dump sites, retained in a lined sludge lagoon and barreled. Still further quantities were emitted as an air pollutant causing soil contaminant concentrations in the city around the production plant. To measure potential groundwater migration, if any, nine test wells were drilled in various locations around the city with particular emphasis on the Kepone burial cell at the landfill and around the sludge holding lagoon.

Results of groundwater monitoring have shown no trends since most samples have been reported as not detected for Kepone. An occasional result at or above the minimum detectable level of 0.02 ppb have not been considered to be significant indicators of groundwater contamination or migration. The Water Control Board will continue its monthly sampling from monitoring wells.

FINFISH MONITORING

The Marine Resources Subcommittee of the Virginia Kepone Task Force was assigned the responsibility to establish and supervise Virginia's monitoring effort with the Water Control Board responsible for finfish collections and the Consolidated Lab for analysis. The sampling program established by the Subcommittee was designed to provide sufficient information for short and long-term problem solution. What is the public health threat? What control actions must be instituted? Can specific species be exempted from limitations?

The sampling program developed was aimed at these questions using the experience of the first year to modify. The locations specified in Table 4 were the selected sample areas using a flexible sample schedule. The sample size desired for each station was 20 replicate samples per species of interest though not always achievable. Where a sample area result in Kepone results above the action level or trending above the action level, a repeat sampling would be accomplished.

We found it necessary to make seasonal adjustments in both location and species. As an example, Shad run in the James River generally from late February to early April. During that period, priority is placed on both sampling and analysis. This year, the River was opened for taking Shad and Herring with responsive sample results being developed to make any further changes in James River closure emergency rules.

As weather warmed, other migratory species are followed into the James River and from the James into the Bay. At the same time, confirmatory samples are taken of James River resident species, such as Bass, to confirm continued high Kepone levels.

As a result of this extensive continuing effort, the James River is open for taking of Catfish, Shad and Herring. Thus far, there have been

Table 4

Kepone Monitoring Stations for Finfish Collections

Station Designation	Location
A	Lower James River between the James River Bridge and the Hampton Roads Bridge-Tunnel
B	James River in the Burwell Bay area
C	James River at the mouth of the Chickahominy River to Hog Island
D	James River in Hopewell area from the Appomattox River to the Benjamin Harrison Bridge
E	James River south of Richmond from Buoy 162 to Deepwater Terminal
F	Chickahominy River from Wilcox Neck to Walker's Dam
G	Lower Chesapeake Bay area from the Chesapeake Bay Bridge-Tunnel
J	Mouth of Rappahannock River
K	James River at Richmond below 14th Street Bridge
N	Mouth of York River
O	Chesapeake Bay at Buoy 4 east of Reedville
P	Chesapeake Bay eastern shore
Q	Chesapeake Bay mouth east of Chesapeake Bay Bridge-Tunnel

Table 5

Areas of Crab Monitoring
Lower James River

1. Vicinity James River Bridge
2. Mouth of Nansemond River
3. Mouth of Elizabeth River
4. Newport News Bar
5. Hampton Bar
6. Willoughby Bay
7. Hampton Flats

no restrictions on taking finfish from the Bay as levels have been consistently below the action level. We envision the necessity for continuing such a program until Kepone levels in the River are reduced, eliminated or Kepone becomes not available for bio-uptake.

SHELLFISH AND CRAB MONITORING

On a monthly basis, crab and oyster samples are collected in the lower James River to verify Kepone levels and the continued assurance of public protection by current emergency rule restrictions. The Marine Resources Subcommittee has devoted greater attention to crabs as oyster concentrations in the James River have remained below the action level of 0.3 ppm.

In the past, crab sampling on a routine basis has been in the areas designated in Table 5 which essentially describes that portion of the James River open for taking of female crabs only. Most of the year, this is an area of predominantly female crabs having Kepone levels below the 0.4 ppm action level. The Subcommittee expanded the monitoring area recently during a migration of male crabs from the tributaries into the lower James and Bay. Males sampled from this migration were found to contain concentration as high as 1.85 ppm and 1.40 ppm. Continued sampling extended to areas of winter dredging will be necessary to describe the extent and degree of hazard resulting from the male migration.

CONCLUSION

Biological and environmental variations have made it essential to adopt and maintain a flexible, seasonally adjusted monitoring program. Based upon results of market sampling, the flexible approach has been successful in achieving the primary objective of protecting the public health.

SESSION IIA

"Kepone Feasibility Study - Corps of Engineers"

CHAIRMAN

Mr. Martin W. Brossman
Deputy Director
Criteria and Standards Division
Office of Water and Hazardous Materials
U.S. Environmental Protection Agency

SPEAKERS

Mr. Roland W. Culpepper
Supervisory Civil Engineer
Norfolk District Corps of Engineers
"Remedial Measures for Capturing, Stabilizing or Removing Kepone in Gravelly Run, Bailey Bay, and Bailey Creek"

Mr. Frank T. Wootton, Jr., P.E.
Chief, Water Resources Planning Branch
Norfolk District Corps of Engineers
"Potential Dredging Technology on the World Market"

Mr. James D. Haluska
Oceanographer
Norfolk District Corps of Engineers
"Environmental Assessment of Engineering Alternatives for Capturing, Stabilizing or Removing Kepone in Gravelly Run, Bailey Bay, and Bailey Creek"

REMEDIAL MEASURES FOR CAPTURING, STABILIZING OR REMOVING KEPONE IN GRAVELLY RUN, BAILEY BAY, AND BAILEY CREEK

BY

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INTRODUCTION

The Corps of Engineers, Norfolk District, is currently conducting preliminary engineering studies to provide an evaluation of alternatives, cost estimates, and limited foundation investigations for capturing, stabilizing, or removing Kepone from Bailey Bay, Bailey Creek, and Gravelly Run. The studies are being conducted under an Interagency Agreement, EPA-IAG-07-01074, with the Environmental Protection Agency. This agreement requires that in addition to the evaluation of alternatives, the Corps will also evaluate all potential dredging technology on the world market and qualitatively assess the environmental impacts for each alternative. This paper outlines the alternatives evaluated to date and does not address dredging technology or environmental impacts. The alternatives have been broken down for the individual areas under consideration and do not necessarily present a complete solution to the problem. After each individual alternative is evaluated, a complete solution will be formulated by combining alternatives for individual areas. It should be noted that the Corps was not to evaluate biological or chemical solutions to the problem which include designing and costing the required treatment facilities.

DESCRIPTION OF STUDY AREA

Bailey Bay, Bailey Creek, and Gravelly Run are located in Hopewell, Virginia and the county of Prince George. Each area is shown on exhibit 1 and is briefly discussed in the following paragraphs.

Bailey Bay is a low-lying area located adjacent to the James River. It is situated between Jordan Point to the east and City Point to the west. It is about 2.4 miles long, 1/2 mile in width, and encompasses about 800 acres. Both Bailey Creek and Gravelly Run discharge into Bailey Bay. The bay for the most part is extremely shallow. At extreme low tides, almost the entire bay bottom is exposed. A few small vegetated islands do exist in the northern portion of the bay.

Bailey Creek, which discharges into Bailey Bay, has a drainage area of about 20 square miles. The creek is 3.2 miles in length from the mouth to Routh 156, about 700 feet wide at the mouth, and about 25 feet wide at Route 156. Two bridges cross the creek, Route 156 and Route 10. Of the 20 square mile drainage area, 14 square miles is above Route 156. Both the east and west bank of Bailey Creek are highly wooded throughout the study area.

Gravelly Run also drains into Bailey Bay and has a drainage area of about 1 square mile. The width of the creek varies from about 50 feet at the mouth to only a small ditch at the Route 10 crossing. The creek has a number of pipeline crossings.

Alternative 1

The first alternative considered was a dam at the mouth of Gravelly Run (exhibit 2). The purpose of the dam was to store all runoff on the Gravelly Run watershed up to and including the 100-Year Flood. The runoff would pass through a treatment facility and be discharged into the James River. Runoff in excess of the 100-Year Flood would be discharged directly into the James River without any treatment. The required capacity of the treatment facility would vary, depending upon the selected retention period. For example, if flood waters were stored for 1-1/2 days, a 50 M.G.D. facility would be needed; whereas, if the waters were stored for 1/2 day, a 150 M.G.D. plant would be required.

The dam would be an earth-filled structure with a top width of 5 feet. The side slopes would be 1 on 3 on the upstream side, and 1 on 2.5 on the downstream side. The height of the dam would be about 23 feet, with a top elevation of 18.4, which includes 3 feet of freeboard. The upstream side of the dam will be protected by riprap to the top and will be protected to elevation 8.5 feet m.s.l. on the downstream side. The 8.5 feet m.s.l. is the elevation of the 100-Year Flood in the James River. A typical section of the dam and spillway is shown on exhibit 3. The reservoir would have a storage capacity of 443 acre-feet and the plan would require acquisition of about 72 acres of land.

In addition to the dam, an emergency spillway would be constructed. The spillway would be designed to accommodate floods up to and including the Standard Project Flood. The spillway would be paved with concrete, would be 100 feet in length, and would have a top elevation of 13.1 feet m.s.l. The cost of this alternative exclusive of the required treatment facility would be about $1.5 million.

Alternative 2

Alternative 2 would likewise involve the construction of an earthen dam (exhibit 4). The elevation of the dam would be 13.4 feet m.s.l., compared to 18.4 feet m.s.l. for alternative 1. In this alternative, no spillway would be required because the flow would be permanently diverted to Bailey Creek and treated in the same manner in which the discharge in Bailey Creek would be treated. In this alternative, as shown, the water would flow to Bailey Creek by gravity. However, if constructed in combination with a dam on Bailey Creek, a pumping station would be required. The diversion works consist of two 8 foot corrugated metal pipes 1,000 feet in length. The cost is estimated to be $2 million.

Alternative 3

Alternative 3 (exhibit 5) would involve sealing the highly contaminated area in the Gravelly Run watershed. It would be accomplished by constructing a control structure at the mouth of Gravelly Run, raising the invert of the existing creek to conform to the control structure, and filling the contaminated area by truck haul. In this alternative, the low-lying area up to elevation 5 feet m.s.l., (including the existing channel) would be covered with 3 feet of fill material. In addition the creek bed would be riprapped to prevent erosion. It would require about 145,000 c.y. of fill material and 14,000 c.y. of riprap protection.

The control structure (exhibit 6) would be constructed by driving concrete "H" piling and placing concrete panels between the piling. The piling would have to be about 40 feet in length for stability. The top elevation of the control structure would be 8 feet m.s.l. with the minimum elevation set at mean sea level to allow for some movement of water during the normal tidal cycle. The cost of this alternative is about $1.8 million.

Alternative 4

Alternative 4 (exhibit 7) is also an alternative to seal the contaminated area. However this plan calls for relocating the existing channel into either a paved channel or a closed conduit.

After preliminary investigations, it was determined that it was more economical to construct a paved channel. A closed conduit would be extremely difficult to construct and support and accommodation of the small tributaries of Gravelly Run might also be difficult. With reference to the paved channel, the benefits derived from sealing the area would be identical to those associated with alternative 3. Due to the fact that no additional benefits would be derived and the cost of a paved channel would be more than the filling alternative, alternative 4 has been eliminated from further consideration.

Alternative 5

Alternative 5 (exhibit 8) calls for dredging a new channel adjacent to the existing channel, sealing the side slopes of the new channel to prevent seepage, and covering the contaminated area as discussed in alternative 3. This alternative, like alternative 4, does not provide benefits over and above those derived in alternative 3. In addition, it would exhibit additional costs associated with dredging a new channel and disposal of the dredged material. It would be constructed similar to alternative 3 in that the bottom of the new channel would have to be riprapped to prevent erosion. For the reasons previously mentioned, this alternative has likewise been eliminated from further consideration.

Alternative 6

This alternative (exhibit 9) would require dredging all contaminated material in Gravelly Run and disposing of the material in a predetermined disposal area. In this alternative, it was assumed that dredging must be accomplished up to elevation 5 feet m.s.l. The depth of dredging would depend on the types of dredging plant utilized. It was determined in the Corps evaluation of potential dredging techniques that the only type of dredge that could be effective in the area are a drag line or bucket dredge, both of which remove a minimum of about 3 feet of material during operation. Dredging to a depth of 3 feet up to elevation 5 feet m.s.l. would require the removal of about 81,000 c.y. of material. In addition, about 20 acres of land would have to be cleared before the dredging operation commenced.

The Corps is presently evaluating a number of disposal areas, including upland and estuarine sites. The final location will be determined at a later date. The selected disposal area will require a treatment facility to treat effluent during the dredging operations. Preliminary cost estimates for this alternative are not available at this time.

Alternative 7

Alternative 7 (exhibit 10) for Bailey Creek is very similar to alternative 1 for Gravelly Run in that a dam would be constructed at the mouth of Bailey Creek to store all runoff from the Bailey Creek watershed for floods up to and including the 100-Year Flood. The runoff would pass through a treatment facility and be discharged into the James River. Runoff in excess of the 100-Year Flood would be discharged directly into the James River without treatment. The required capacity of the treatment facility would depend upon the selected retention period. For example, if the flood waters were stored for 12 days, a 50 M.G.D. Plant would be needed; whereas, if the flood waters were stored for 4 days, a 150 M.G.D. plant would be required.

The dam would be an earth-filled structure with a top width of 15 feet. The side slopes would be 1 on 3 on the upstream side and 1 on 2.5 on the downstream side. The height of the dam would be about 23 feet, with a top elevation of 18.4 feet m.s.l., which includes 3 feet of freeboard. Like the proposed dam on Gravelly Run, the dam on Bailey Creek would be protected with riprap to the top on the upstream side and to elevation 8.5 feet m.s.l. on the downstream side. In addition, the dam will contain a slurry cutoff in the center to prevent seepage of the contaminated waters into the James River. The resulting reservoir would have a storage capacity of 7,150 acre-feet and the plan would require the acquisition of about 1,060 acres of land. In addition to the dam, an emergency spillway would be constructed. The spillway would be designed to accommodate floods up to and including the Standard Project Flood. The spillway would be paved with concrete, would be 100 feet in length, and would have a top elevation of 15.9 feet m.s.l. A typical section of the dam and spillway is shown in exhibit 11. The cost of this alternative, exclusive of the required treatment facility, would be approximately $14 million.

Alternative 8

Alternative 8 (exhibit 12) for Bailey Creek would require sealing the highly contaminated area in Bailey Creek similar to that proposed in alternative 3 for Gravelly Run. It would likewise be accomplished by constructing a control structure (exhibit 13) at the mouth of Bailey Creek, raising the invert of the existing creek, and filling the contaminated area by truck haul. The contaminated area would be filled up to elevation 5 feet m.s.l. to a depth of 3 feet. In addition the creek bed would be riprapped to prevent erosion. This alternative would require about 2.2 million c.y. of fill material and 156,000 c.y. of riprap protection. The cost would be approximately $20 million.

Alternative 9

As for Gravelly Run, consideration was given to relocating the existing channel in Bailey Creek into either a paved channel or a closed conduit (exhibit 14) and covering the contaminated area as discussed in alternative 8. After preliminary investigations, it was determined that it was more economical to construct a paved channel. A closed conduit would be extremely difficult to construct and support and to accommodation of the small tributaries of Bailey Creek might also be difficult. With reference to the paved channel, the benefits derived from sealing the area would be identical to those associated with alternative 8. Due to the fact that no additional benefits would be derived and the cost of a paved channel would be more than the filling alternative, alternative 9 has been eliminated from further consideration.

Alternative 10

Alternative 10 (exhibit 15) would require dredging a new channel adjacent to the existing channel in Bailey Creek, sealing the side slopes of the new channel to prevent seepage, and covering the contaminated area as discussed in alternative 8. This alternative, like alternative 9, does not provide benefits over and above those derived in alternative 8. In addition, it would exhibit additional costs associated with dredging a new channel and disposal of the dredged material. It would be constructed similar to alternative 8 in that the bottom of the new channel would have to be riprapped to prevent erosion. Alternative 10 has likewise been eliminated from further consideration.

Alternative 11

Alternative 11 (exhibit 16) would require dredging all contaminated material in Bailey Creek and pumping it into a predetermined disposal area. This alternative would require a treatment facility at the disposal area to treat all effluent during the dredging operations. The cost of this alternative will be based on dredging Bailey Creek up to the elevation of 5 feet m.s.l. to a depth of at least 3 feet. As in alternative 6, the type of dredge to be used would be the drag line or bucket dredge. This alternative would require clearing about 410 acres and excavating about 2.2 million c.y. of material. Preliminary cost estimates are not available at this time.

Alternative 12

In evaluating alternative 7, it was proposed that the unpolluted runoff upstream from the city-owned sewage treatment plant be diverted to an adjacent watershed, thereby reducing the size of the downstream dam and the associated treatment facility. Alternative 12 (exhibit 17) and 12A deal with the proposed diversion with the only difference being the method of transferring the runoff from one watershed to another. Alternative 12 would require a dam to be constructed upstream of Route 156 to divert all floods up to an including the 100-Year Flood to Chappell Creek. The dam would, as in previous alternatives, be an earth-filled structure with a top width of 10 feet. The side slopes would be 1 on 3 on the upstream side and 1 on 2.5 on the downstream side. The height of the dam would be about 40 feet with a top elevation of 45 feet m.s.l., which includes 3 feet of freeboard. The resulting reservoir will have a storage capacity of 3,800 acre-feet, and the plan would require the acquisition of about 1,405 acres of land.

In addition to the dam, an emergency spillway would be constructed. The spillway would be designed to accommodate floods up to and including the Standard Project Flood. The spillway would be paved with concrete, would be 200 feet in length, and would have a top elevation of 37 feet m.s.l. A typical section of the spillway and dam is shown on exhibit 18. The diversion facility would consist of a pumping station with a total capacity of 650 c.f.s. and two welded steel pipes running to Chappell Creek, a distance of about 17,000 feet. The cost of this alternative is approximately $35 million.

Alternative 12A

As previously stated, alternative 12A (exhibit 19) is another alternative to divert the unpolluted runoff from the upper reaches of Bailey Creek to an adjacent watershed. The dam structure involved would be the same as that presented in alternative 12. The diversion works consist of two welded steel pipes, 10 feet in diameter and about 17,000 feet in length. The pipe line would be laid adjacent to the existing creek and the unpolluted water from the reservoir would flow by gravity to the James River. The cost of diversion by gravity would be about $23 million.

Alternative 13

Alternative 13 (exhibit 20) would require dredging the highly contaminated material in Bailey Bay and disposing of the material in a confined disposal area. The disposal area would either be an upland or estuarine site depending upon the results of ongoing studies. The results of the Corps investigations of potential dredging techniques indicates that the depth of dredging that could be expected in Bailey Bay is 3 feet. This figure is not based on the depth of Kepone but due to the depth of water required for the dredging plant. Using a dredging depth of 3 feet and assuming that all material with Kepone concentrations of .3 p.p.m. will be removed, the required excavation would be about 2.8 million c.y. However, if .1 p.p.m. was used as a standard, the required excavation would increase 1.5 million c.y. resulting in the removal of 4.3 million c.y. from Bailey Bay.

Alternative 14

Alternative 14 (exhibit 21) would require constructing a levee from a point 1 mile east of City Point to Jordan Point, a distance of about 14,250 feet. This would allow for the containment of all runoff from Bailey Creek and Gravelly Run. The alignment shown takes into account that the toe of the levee should be at least 1,000 feet from the existing James River Channel. The levee would contain an emergency spillway, and the plan would require a treatment facility.

The levee would be constructed with a design elevation of 10 feet m.s.l. This would provide protection from flooding from the James River by the 100-Year Flood tide with 1-1/2 feet of freeboard. Construction of the levee would consist of spreading a sand blanket over the existing bottom. After the sand has been raised to a sufficient elevation, the area would then be raised to the required elevation with an impervious fill material. To prevent seepage, a 3-foot wide slurry cutoff trench would be constructed to a depth of 10 feet below the hydraulic fill line. In addition, riprap would be placed on the outside lower slope to prevent erosion. The cost of this alternative, exclusive of the treatment facility, would be about $8 million.

Alternative 15

Alternative 15 (exhibit 22) is one of the original 18 alternatives in which consideration is given to treating the entire area. The proposal would require contructing a dam at the mouth of Gravelly Run and diverting the discharge from Gravelly Run to Bailey Bay similar to the plans in alternative 2. In addition to the dam, a pumping station would be required. A dam would also be constructed at the mouth of Bailey Creek similar to that proposed in alternative 7 except that the elevation would be increased to 20 feet m.s.l. Bailey Bay would be dredged and the material deposited behind the dam on Bailey Creek. the total storage capacity of the two dams would be about 8,700 acre-feet, and the plan would require the acquisition of about 930 acres of land.

In addition to the two dams, a treatment facility would be required. Like the other alternatives considering dams, the size of the treatment facility would depend on the retention period selected. For example, if a 19-day retention period was selected, a 100 M.G.D. plant would be required; whereas, if the retention period was 12 days, a 150 M.G.D. plant would be required. The cost of the alternative, exclusive of dredging and treatment facilities, is in excess of $21 million.

Alternative 16

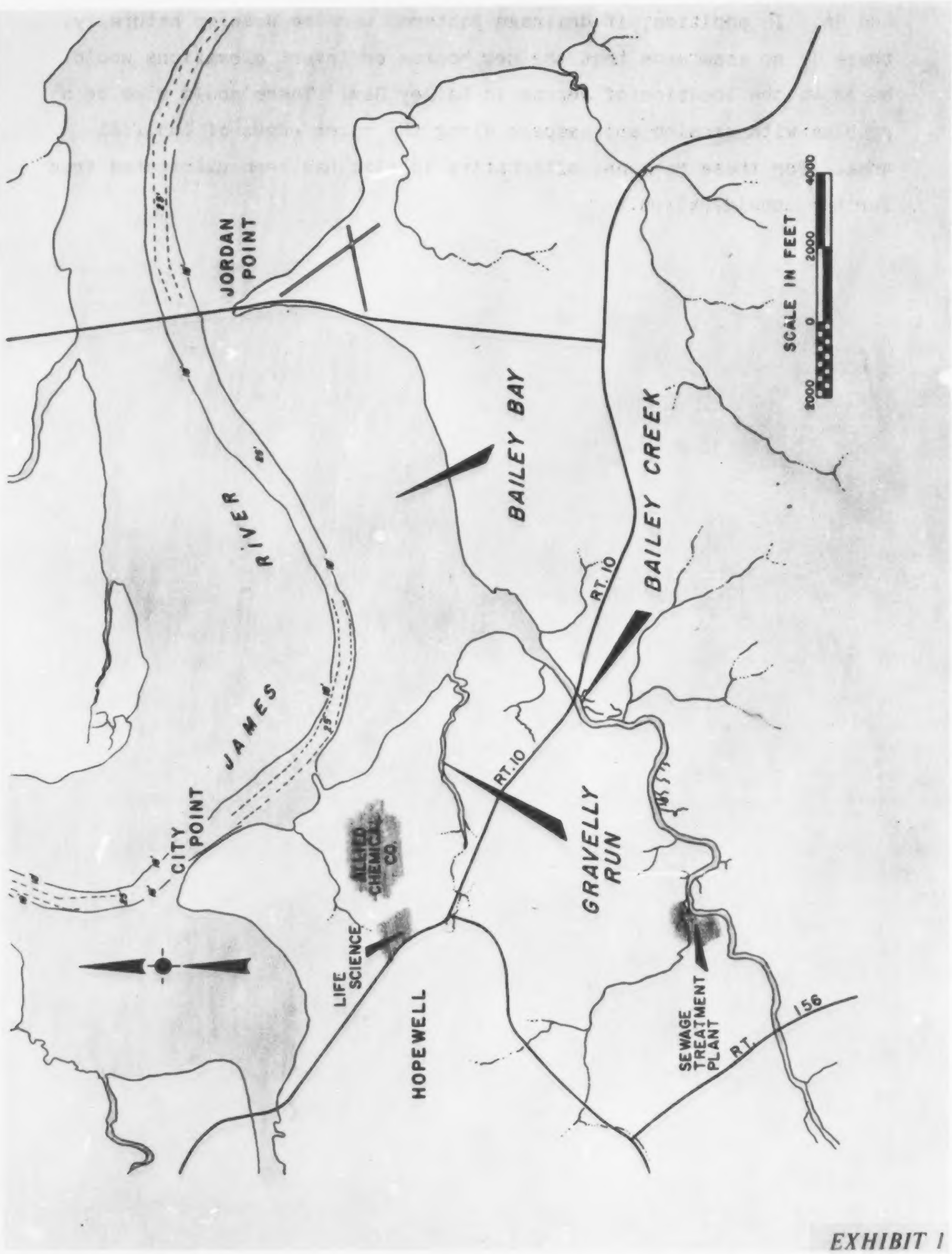
Alternative 16 (exhibit 23) would require construction of a levee from a point 1 mile east of City Point to Jordon Point, as in alternative 14. The difference between alternative 16 and 14 is that the area behind the levee would be used as a disposal area for maintenance dredging of the James River and possibly could be used for placement of other contaminated material adjacent to the study area. The thought of the conception of this alternative is that the levee height for the two alternatives (14 & 16) would most likely be different. However, to prevent flooding of the disposal area by the 100-Year Flood in the James River, the height of the levee must be the same as in alternative 14. The cost of this alternative would likewise be about $8 million.

Alternative 17

Alternative 17 likewise provides a complete solution to the Kepone problem; whether or not it is practical and feasible will be determined at a later date. The plan would require construction of a levee from Jordan Point to the east side of Bailey Creek (exhibit 24) and use of the confined area as a disposal area for dredging the remainder of Bailey Bay and all contaminated areas in Bailey Creek and Gravelly Run. A treatment facility would have to be constructed to treat the effluent from the disposal area until dredging of each area is complete. The disposal area would then be sealed with an impervious blanket, covered with topsoil, and planted with grass. The levee would be constructed in the same manner as the other levees discussed. However, it would be constructed to about elevation 15 m.s.l. to provide the required storage capacity.

Alternative 18

This alternative (exhibit 25) would require covering the entire contaminated area with an impervious blanket to a depth which would allow natural drainage patterns in the area to develop. However, there are no known methods to fill the area with impervious material unless the area is diked to control sedimentation downstream. If the area were diked, this alternative would be similar to alternative 14 and 16. In addition, if drainage patterns were to develop naturally, there is no assurance that the new bottom or invert elevations would be above the location of Kepone in Bailey Bay. There could also be a problem with erosion and seepage along the outer edges of the fill area. For these reasons, alternative 18 also has been eliminated from further consideration.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JAMES RIVER
CITY POINT
BAILEY BAY
BAILEY CREEK
RT. 10
RT. 10
GRAVELLY RUN
ALLIED CHEMICAL CO.
LIFE SCIENCE
HOPEWELL
SEWAGE TREATMENT PLANT
RT. 156
SCALE IN FEET
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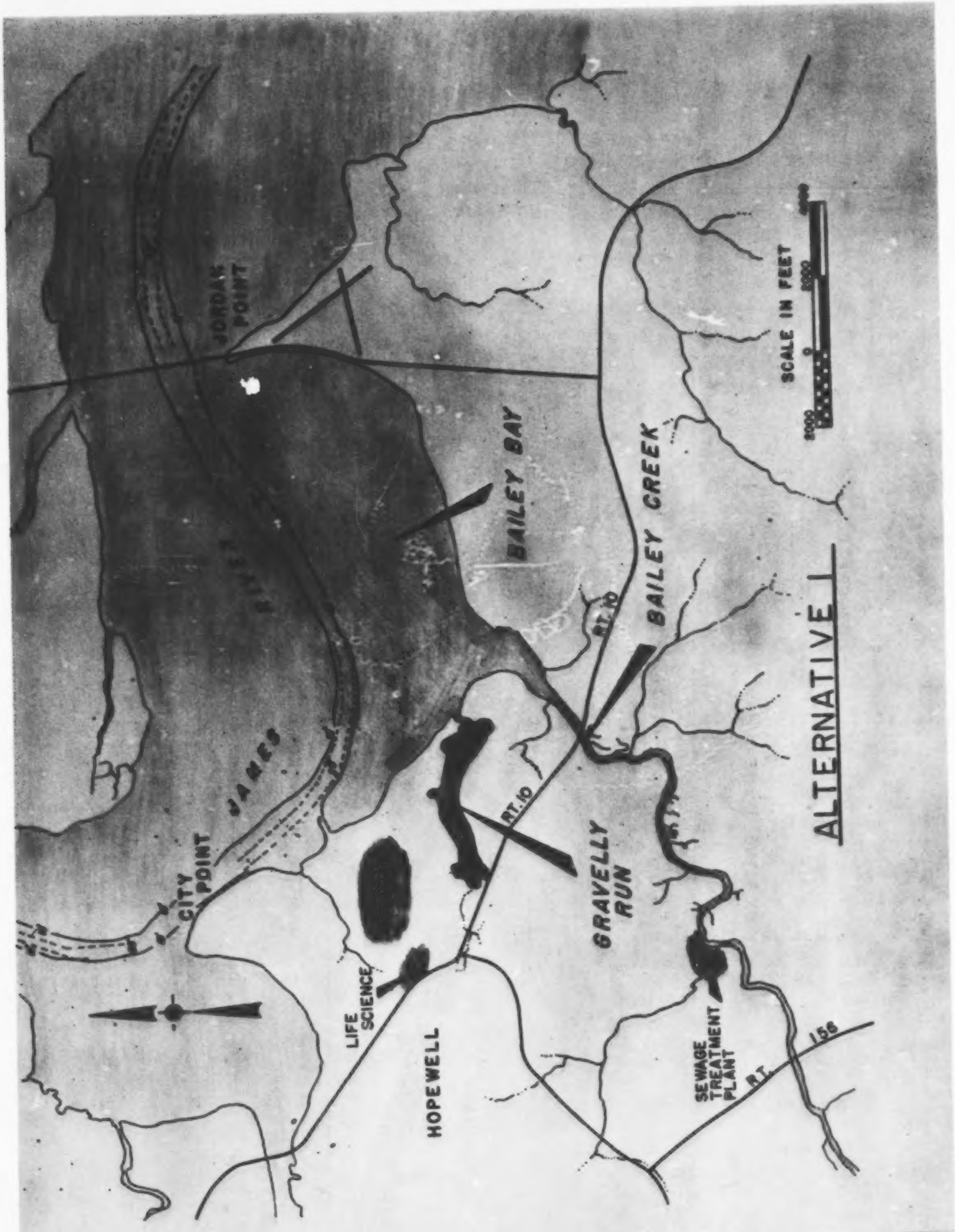
EXHIBIT I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CITY POINT
BAILEY BAY
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RT. 10
GRAVELLY RUN
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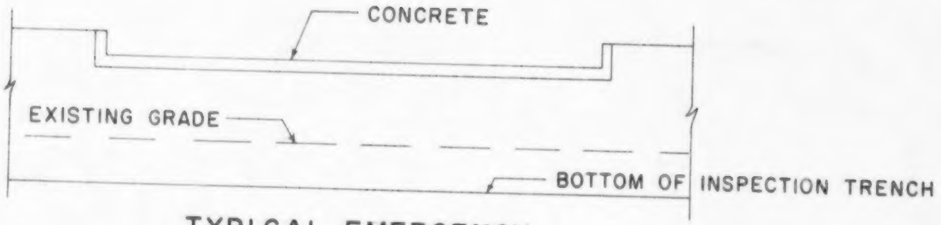
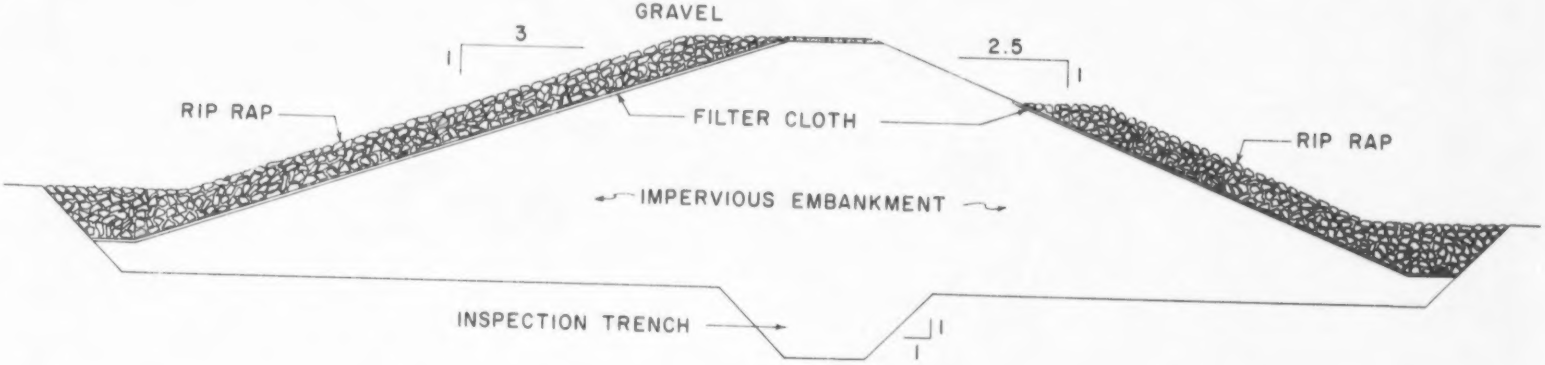
ALTERNATIVE I

EXHIBIT 2


CONCRETE
EXISTING GRADE
BOTTOM OF INSPECTION TRENCH

TYPICAL EMERGENCY
SPILLWAY SECTION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3
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2.5
1
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FILTER CLOTH
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IMPERVIOUS EMBANKMENT
INSPECTION TRENCH
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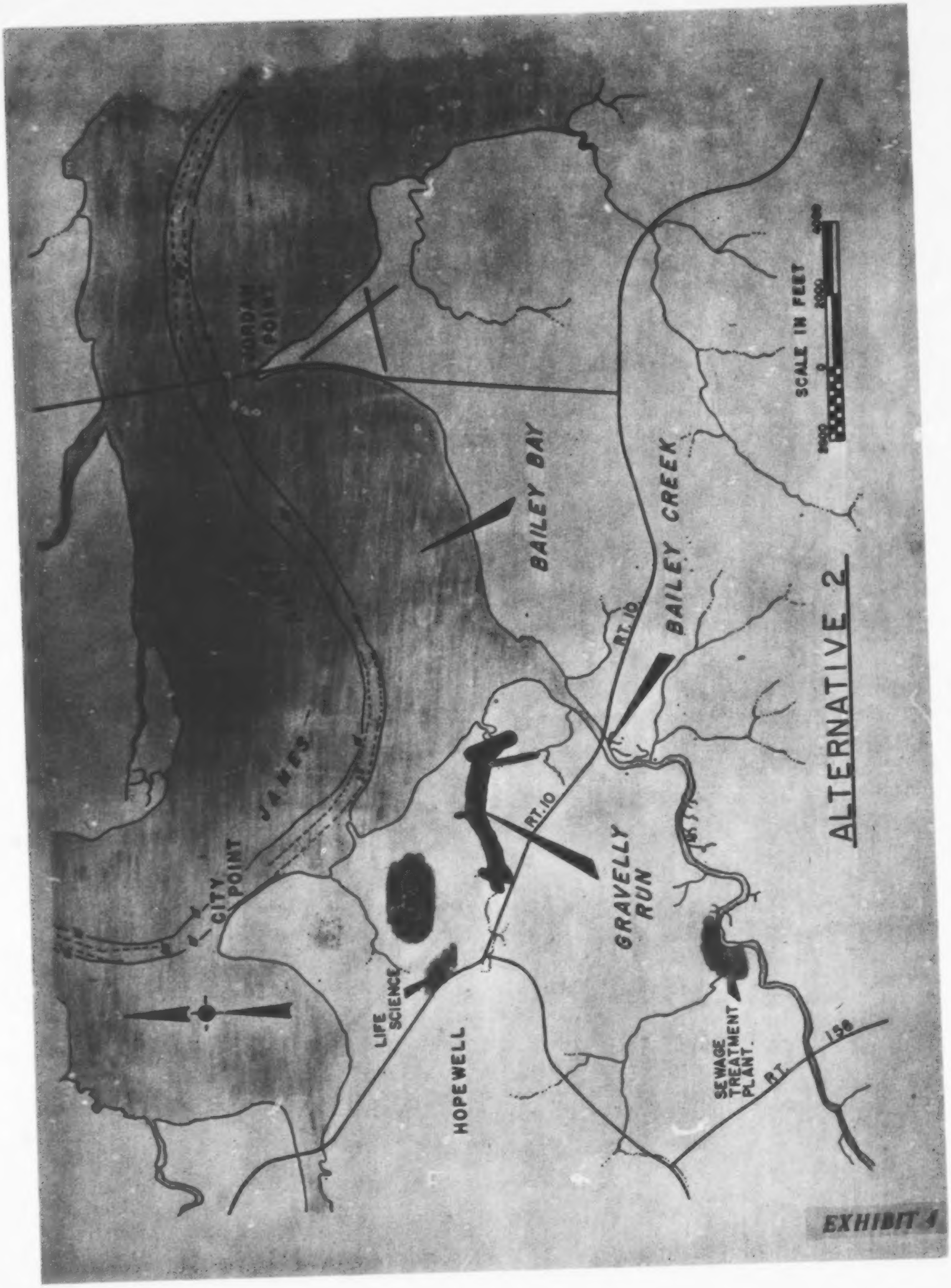
1

TYPICAL DAM SECTION
AT MOUTH OF
GRAVELLY RUN

EXHIBIT 3


ALTERNATIVE 2
EXHIBIT 4
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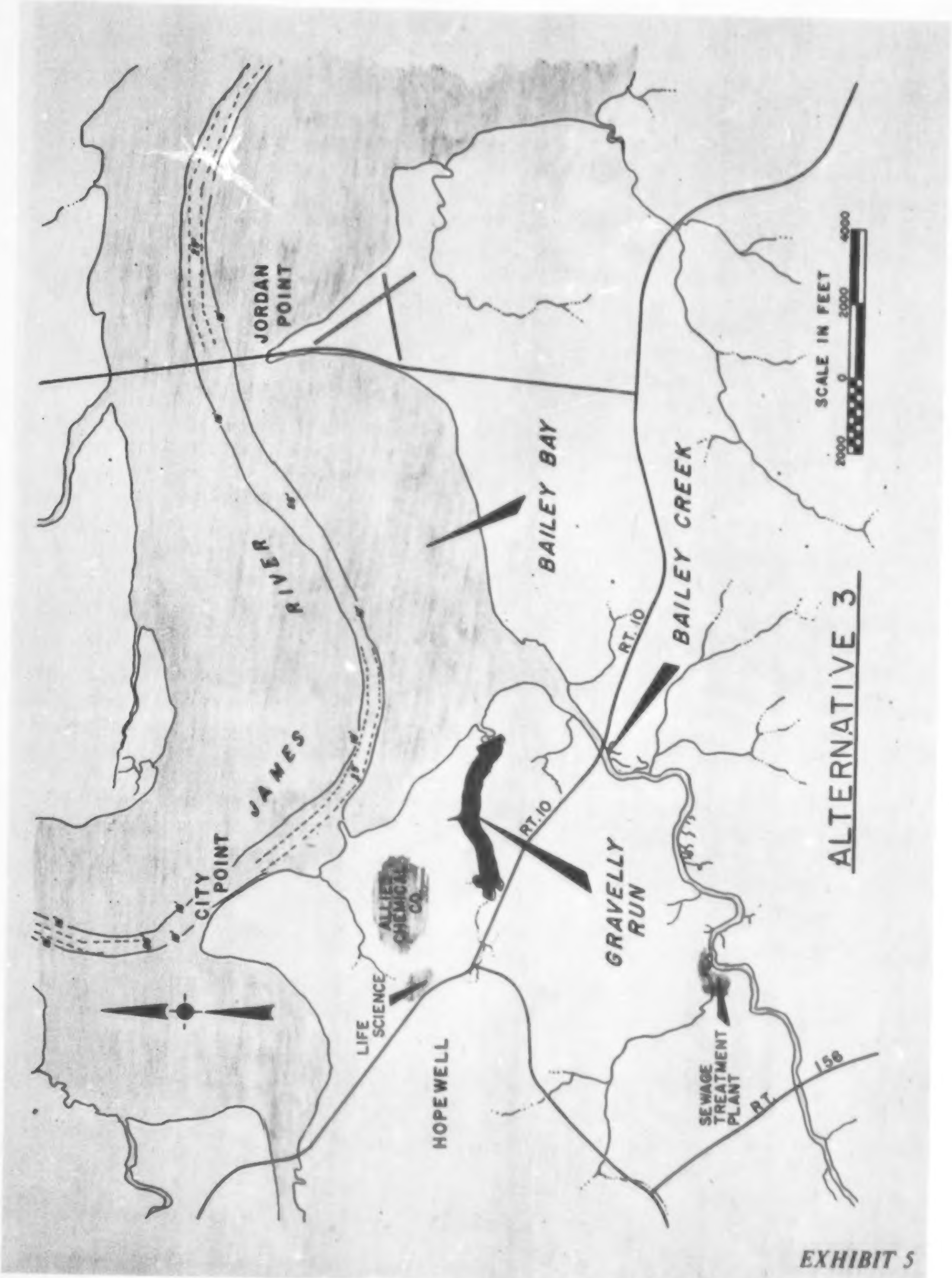
BAILEY BAY
BAILEY CREEK
JAMES
CITY POINT
RT. 10
GRAVELLY RUN
LIFE SCIENCE
HOPEWELL
SEWAGE TREATMENT PLANT.
RT. 156
SCALE IN FEET
2000
0
2000
4000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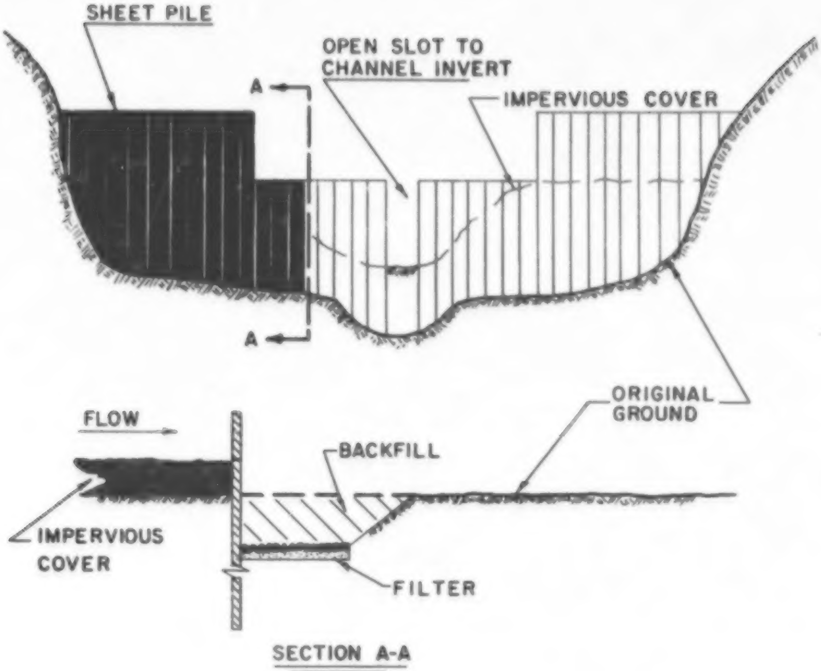
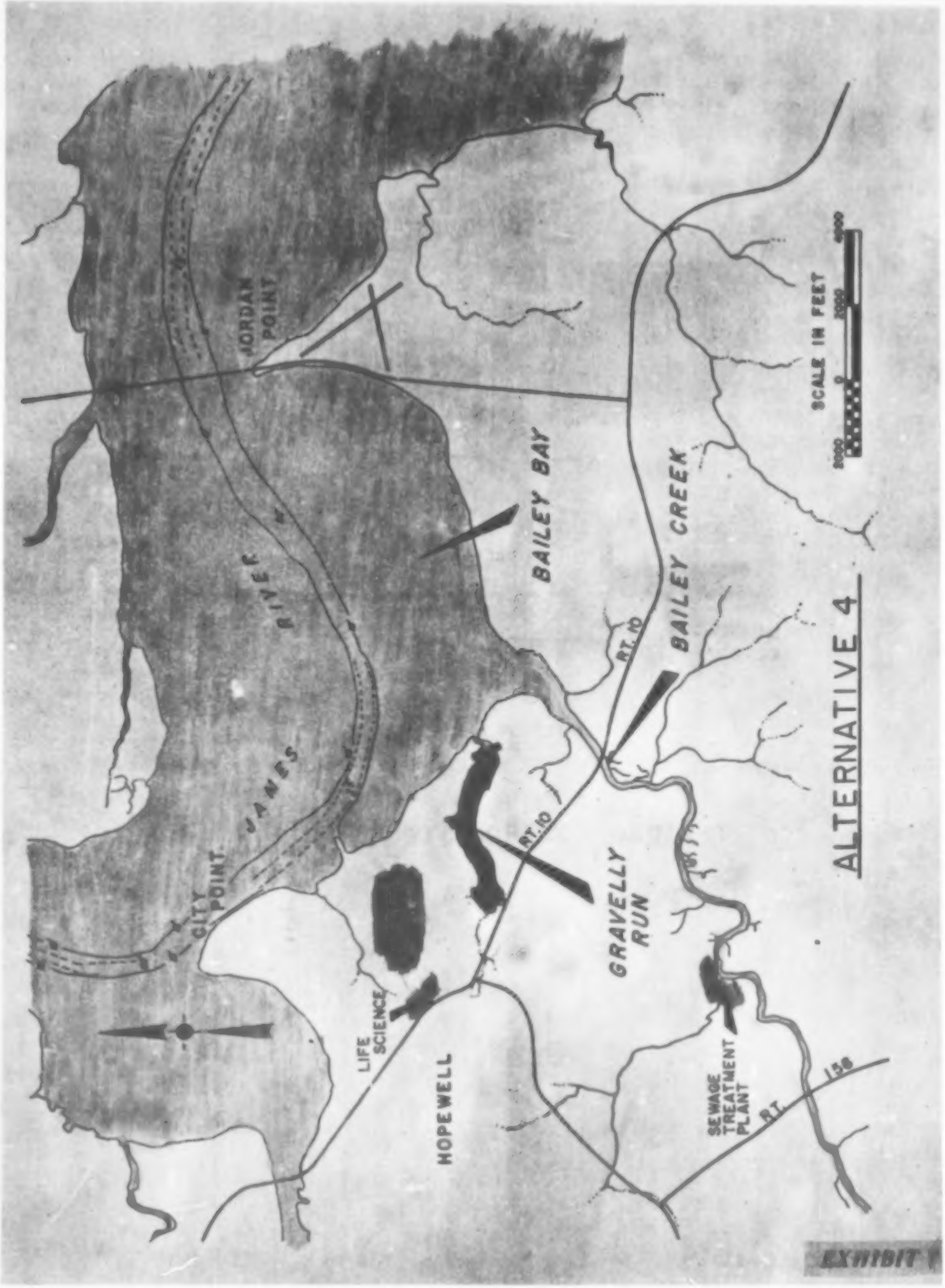
JORDAN POINT
BAILEY BAY
BAILEY CREEK
RT. 10
RT. 10
GRAVELLY RUN
ALLIED CHEMICAL CO.
LIFE SCIENCE
HOPEWELL
SEWAGE TREATMENT PLANT
RT. 156
SCALE IN FEET
2000
0
2000
4000

EXHIBIT 5


SHEET PILE
OPEN SLOT TO CHANNEL INVERT
IMPERVIOUS COVER
A
A
ORIGINAL GROUND
FLOW
BACKFILL
IMPERVIOUS COVER
FILTER
SECTION A-A

TYPICAL CONTROL STRUCTURE

EXHIBIT 6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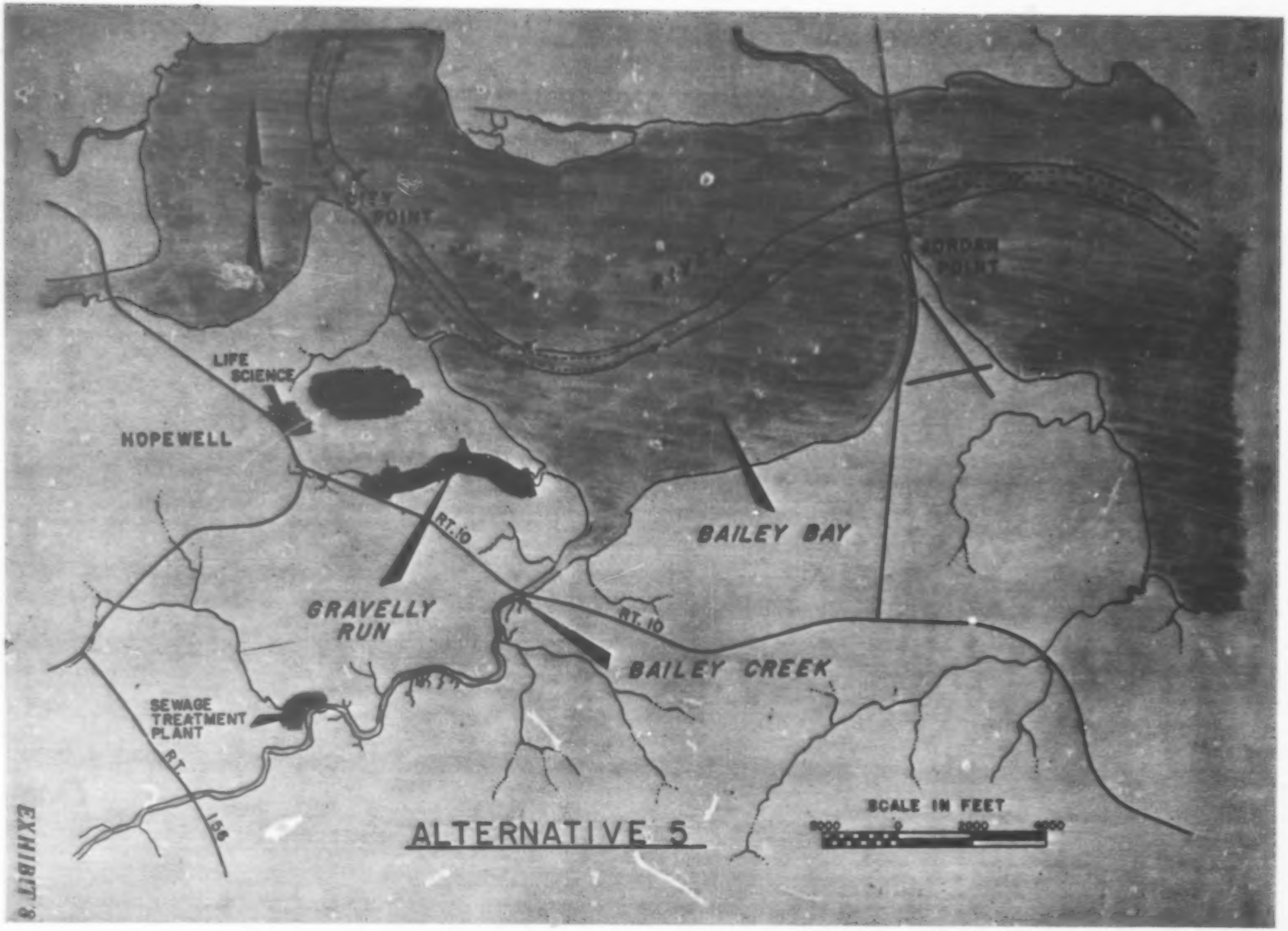
JORDAN POINT
BAILEY BAY
BAILEY CREEK
RT. 10
RT. 10
GRAVELLY RUN
LIFE SCIENCE
HOPEWELL
SEWAGE TREATMENT PLANT
RT. 156
SCALE IN FEET
2000
0
2000
4000
EXHIBIT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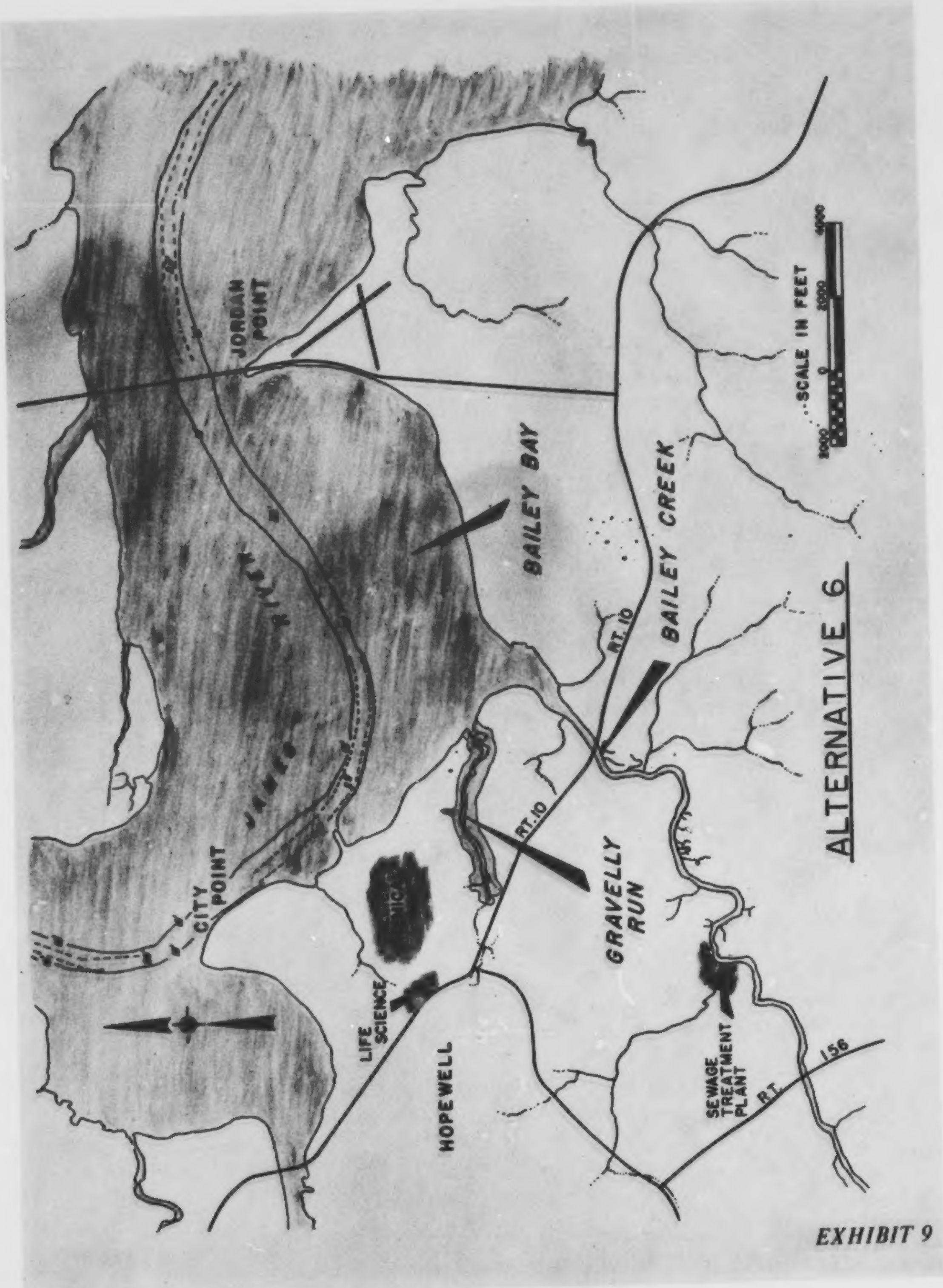
JORDAN POINT
LIFE SCIENCE
HOPEWELL
RT. 10
BAILEY BAY
GRAVELLY RUN
RT. 10
BAILEY CREEK
SEWAGE TREATMENT PLANT
RT. 156
SCALE IN FEET
2000
0
2000
4000

ALTERNATIVE 5

EXHIBIT 8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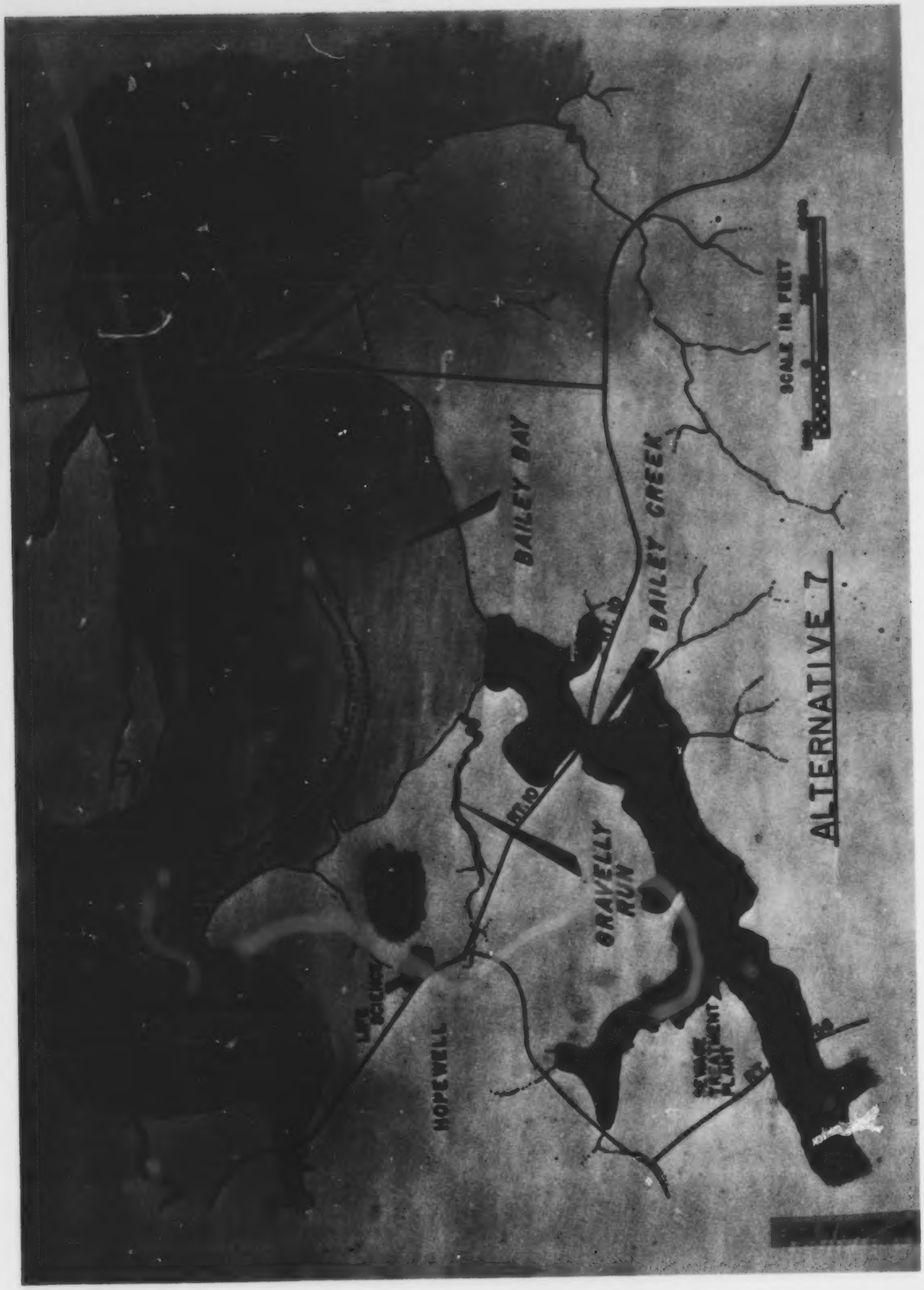
BAILEY CREEK
RT. 10
RT. 10
JAMES RIVER
CITY POINT
GRAVELLY RUN
LIFE SCIENCE
HOPEWELL
SEWAGE TREATMENT PLANT
RT. 156
SCALE IN FEET
2000
0
2000
4000

ALTERNATIVE 6

EXHIBIT 9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BAILEY CREEK
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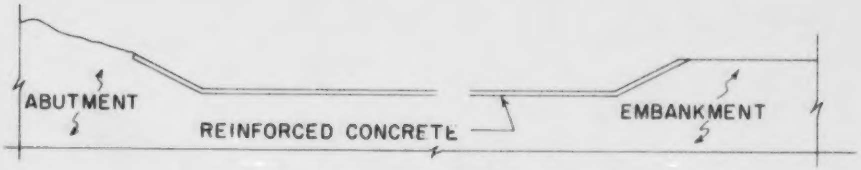
LIFE SCIENCE
HOPEWELL
SEWAGE TREATMENT PLANT
SCALE IN FEET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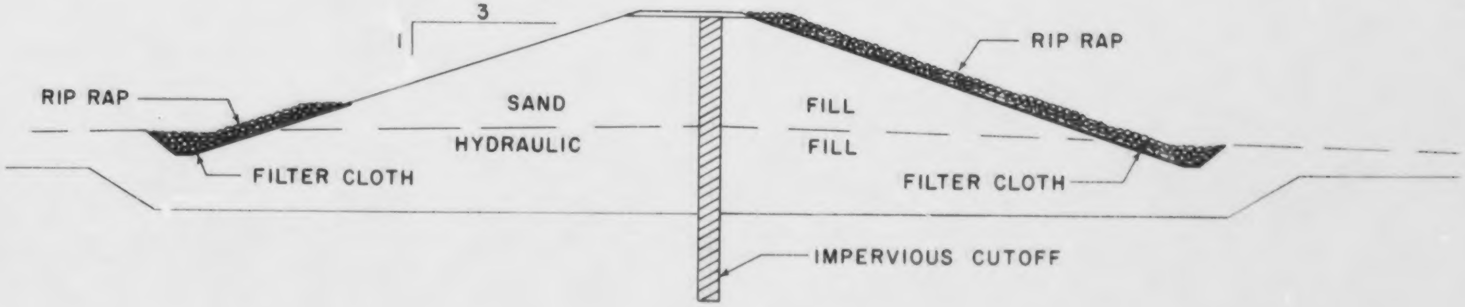
REINFORCED CONCRETE
EMBANKMENT

TYPICAL EMERGENCY
SPILLWAY SECTION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SAND
HYDRAULIC
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FILL
FILL
RIP RAP
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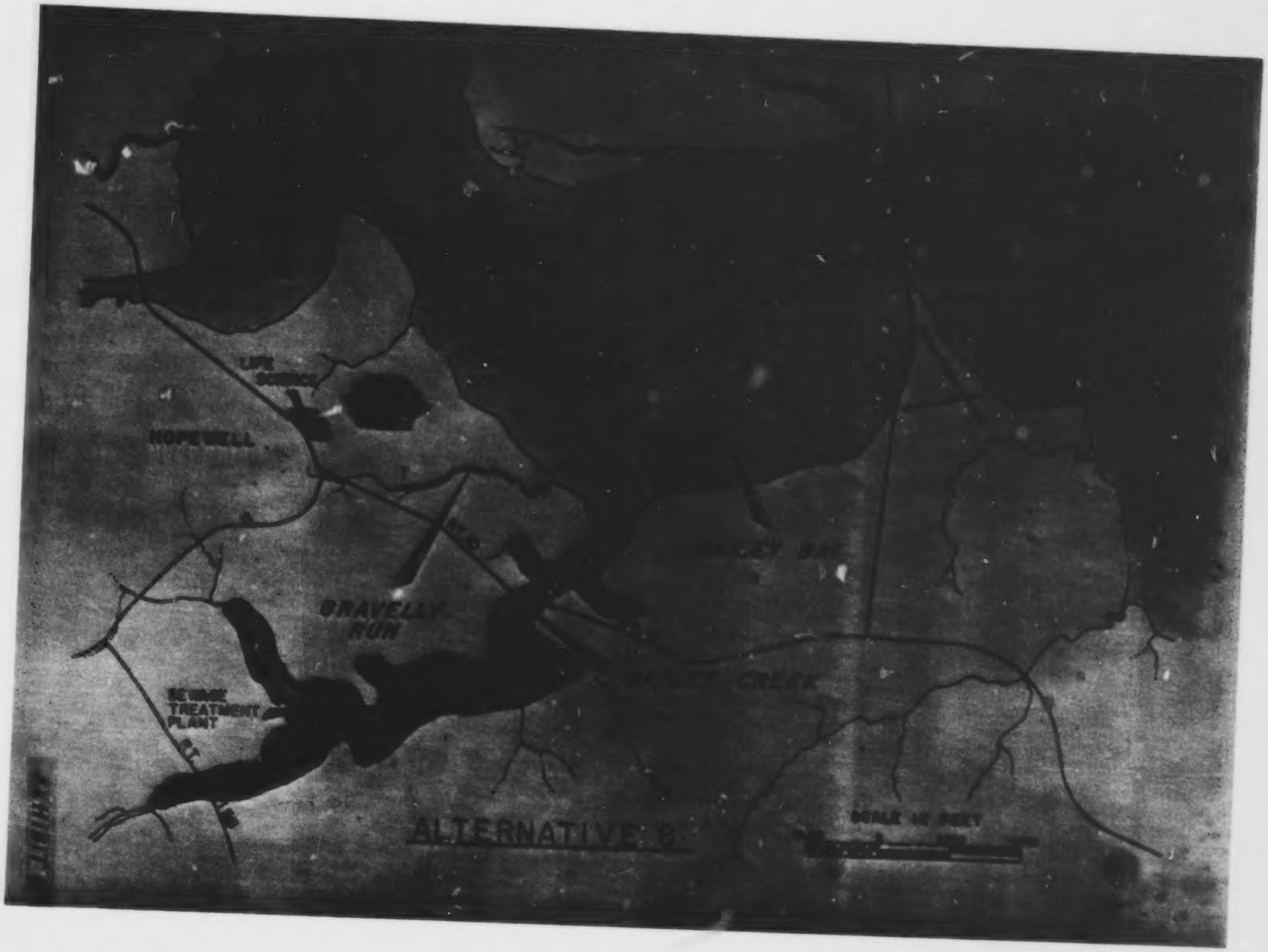
IMPERVIOUS CUTOFF

TYPICAL DAM SECTION
AT MOUTH OF
BAILEY CREEK

EXHIBIT 11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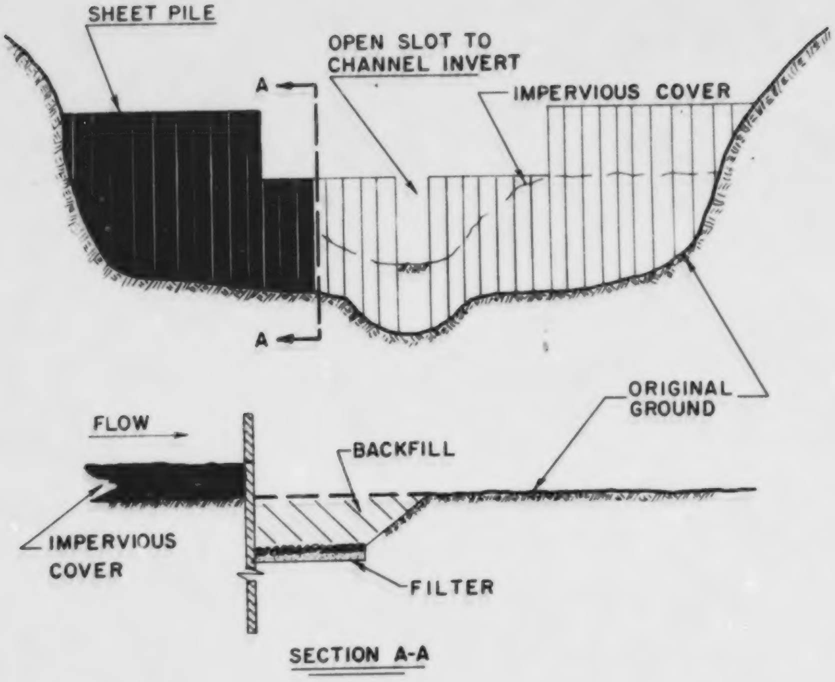
HOPEWELL
GRAVELLY RUN
SEWAGE TREATMENT PLANT
BAY
CREEK
SCALE IN FEET

ALTERNATIVE B

EXHIBIT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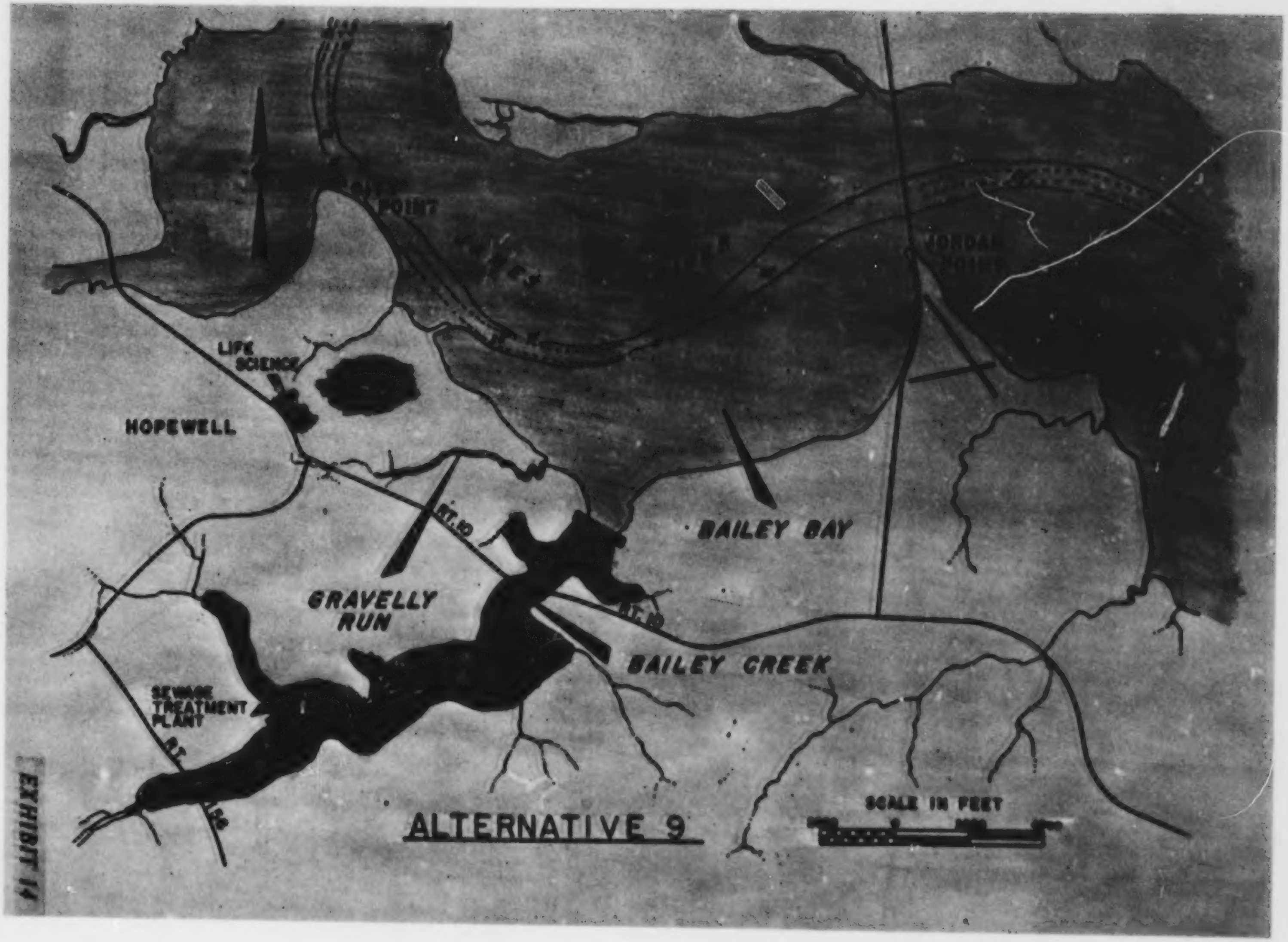
OPEN SLOT TO CHANNEL INVERT
IMPERVIOUS COVER
A
A
ORIGINAL GROUND
FLOW
BACKFILL
IMPERVIOUS COVER
FILTER
SECTION A-A

TYPICAL CONTROL STRUCTURE

EXHIBIT 13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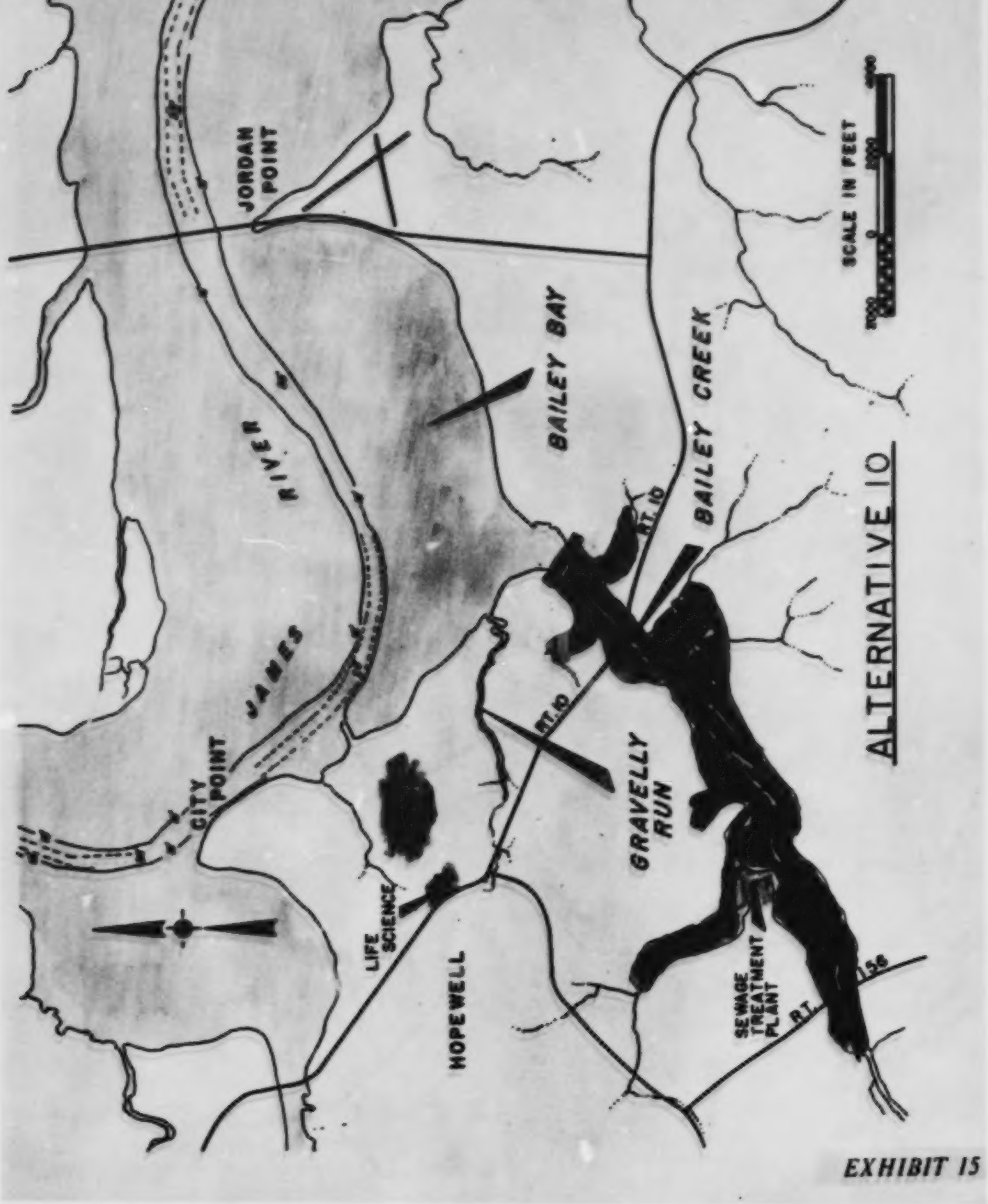
JAMES
JORDAN POINT
LIFE SCIENCE
HOPEWELL
RT. 10
BAILEY BAY
GRAVELLY RUN
RT. 10
BAILEY CREEK
SEWAGE TREATMENT PLANT
RT. 156
SCALE IN FEET

ALTERNATIVE 9

EXHIBIT 14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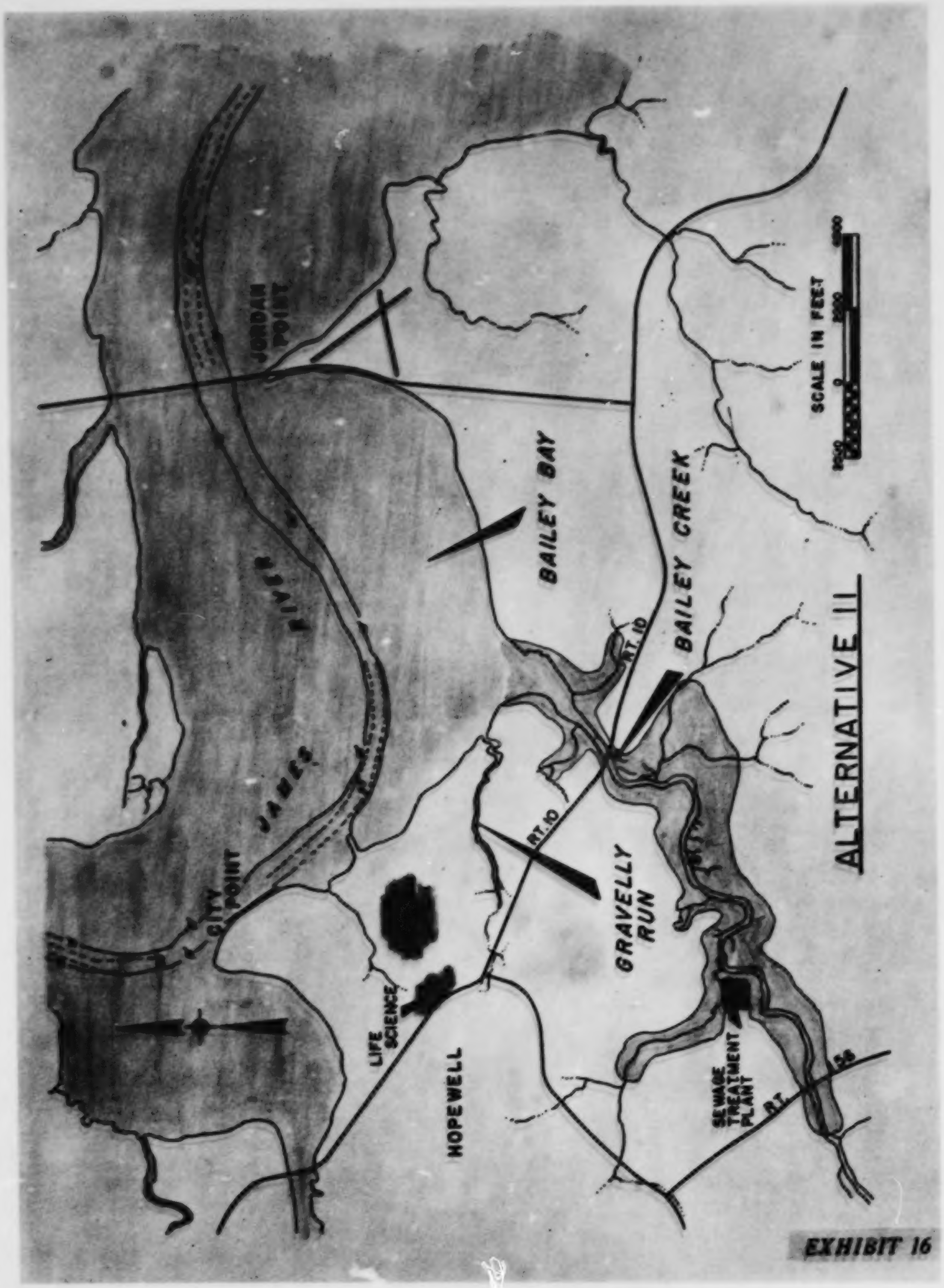
JAMES
RIVER
CITY POINT
BAILEY BAY
BAILEY CREEK
RT. 10
RT. 10
GRAVELLY RUN
LIFE SCIENCE
HOPEWELL
SEWAGE TREATMENT PLANT
RT. 156
SCALE IN FEET
1000
0
1000
2000

ALTERNATIVE 10

EXHIBIT 15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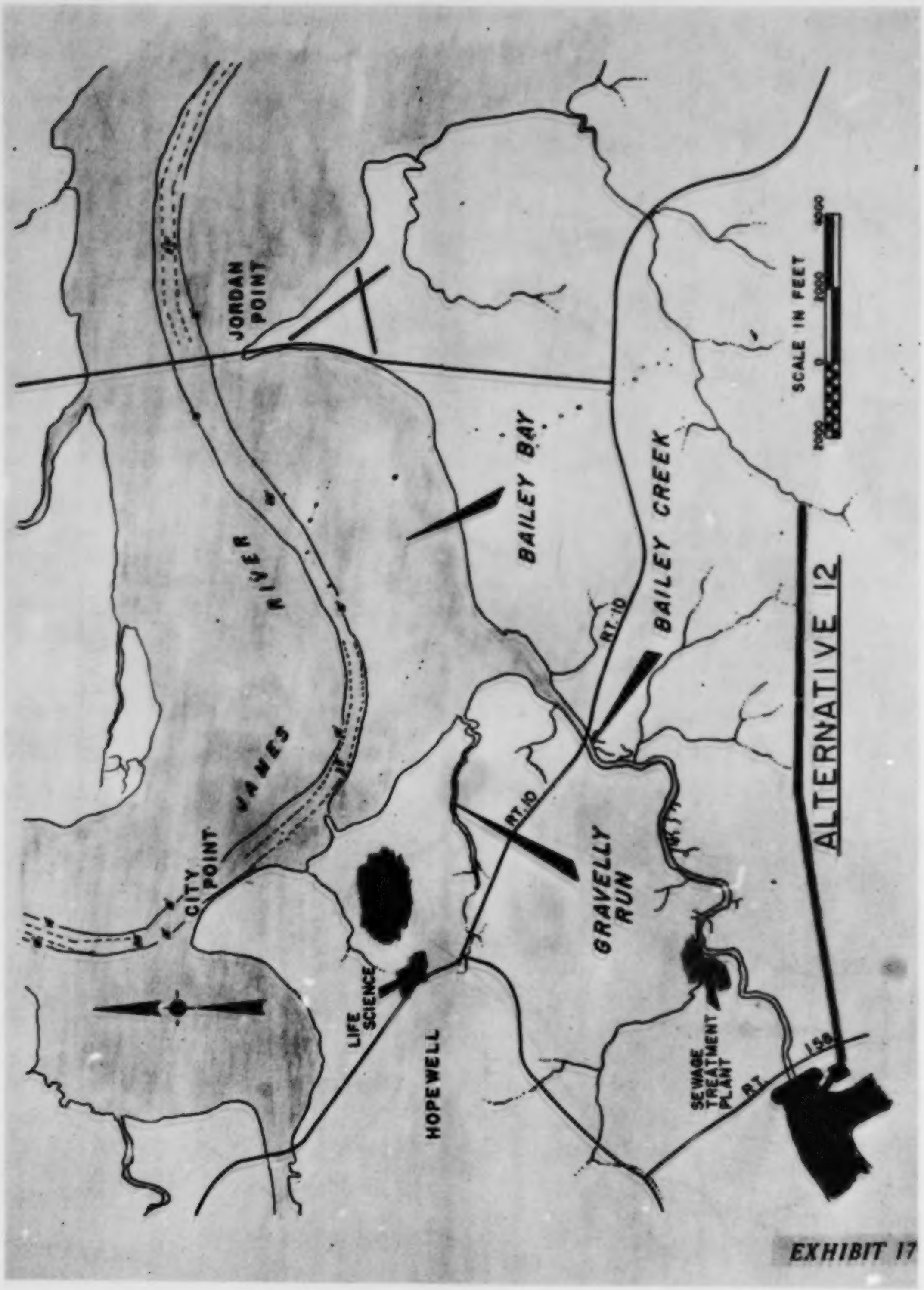
JORDAN POINT
CITY POINT
BAILEY BAY
BAILEY CREEK
RT. 10
GRAVELLY RUN
LIFE SCIENCE
HOPEWELL
SEWAGE TREATMENT PLANT
RT. 156
SCALE IN FEET
1250
0
2500
5000

ALTERNATIVE II

EXHIBIT 16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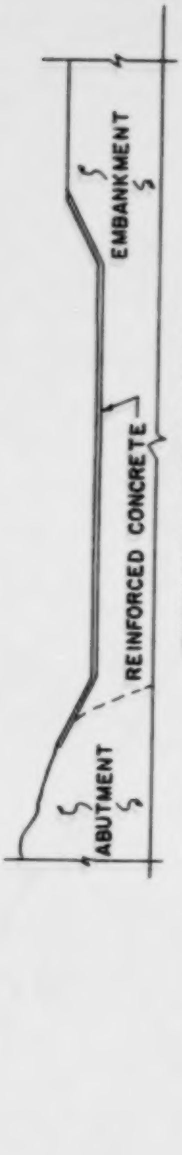
BAILEY BAY
BAILEY CREEK
RT. 10
RT. 10
JAMES RIVER
CITY POINT
GRAVELLY RUN
LIFE SCIENCE
HOPEWELL
SEWAGE TREATMENT PLANT
RT. 156
SCALE IN FEET
2000
0
2000
4000

ALTERNATIVE 12

EXHIBIT 17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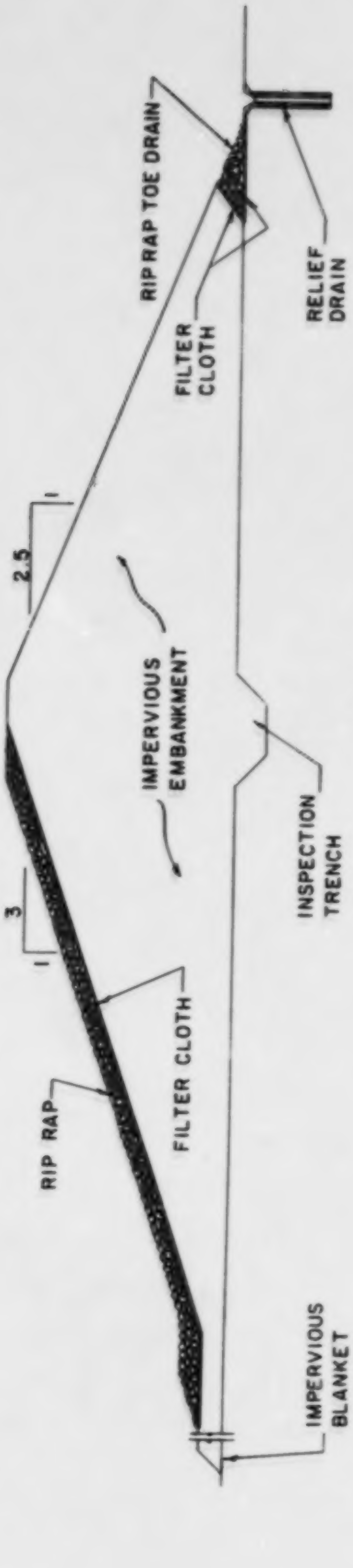
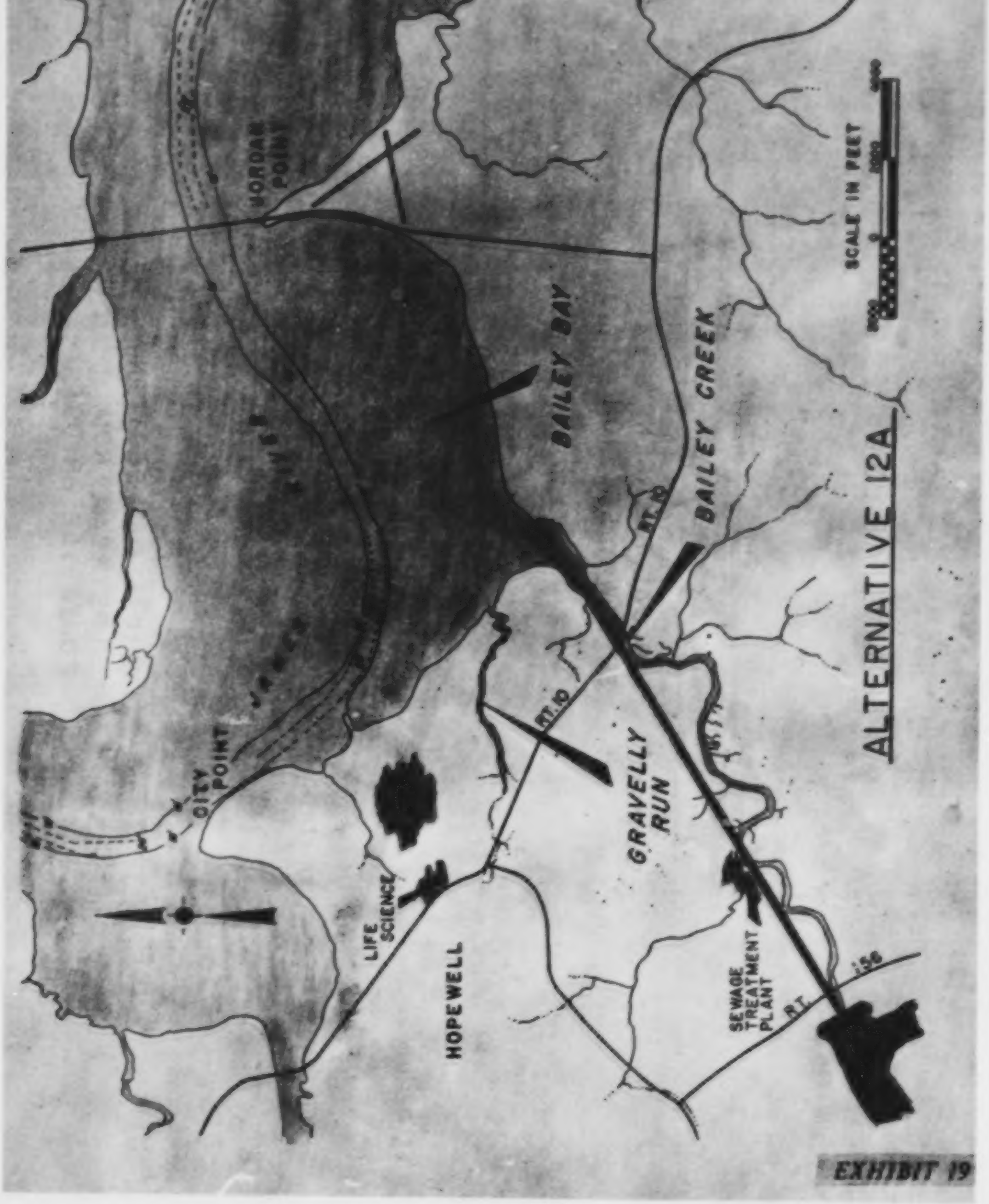
REINFORCED CONCRETE
EMBANKMENT

TYPICAL EMERGENCY SPILLWAY SECTION


RIP RAP
FILTER CLOTH
1
3
IMPERVIOUS EMBANKMENT
2.5
1
INSPECTION TRENCH
FILTER CLOTH
RIP RAP TOE DRAIN
RELIEF DRAIN
IMPERVIOUS BLANKET

TYPICAL DAM SECTION UPSTREAM FROM ROUTE 156 BRIDGE

EXHIBIT 18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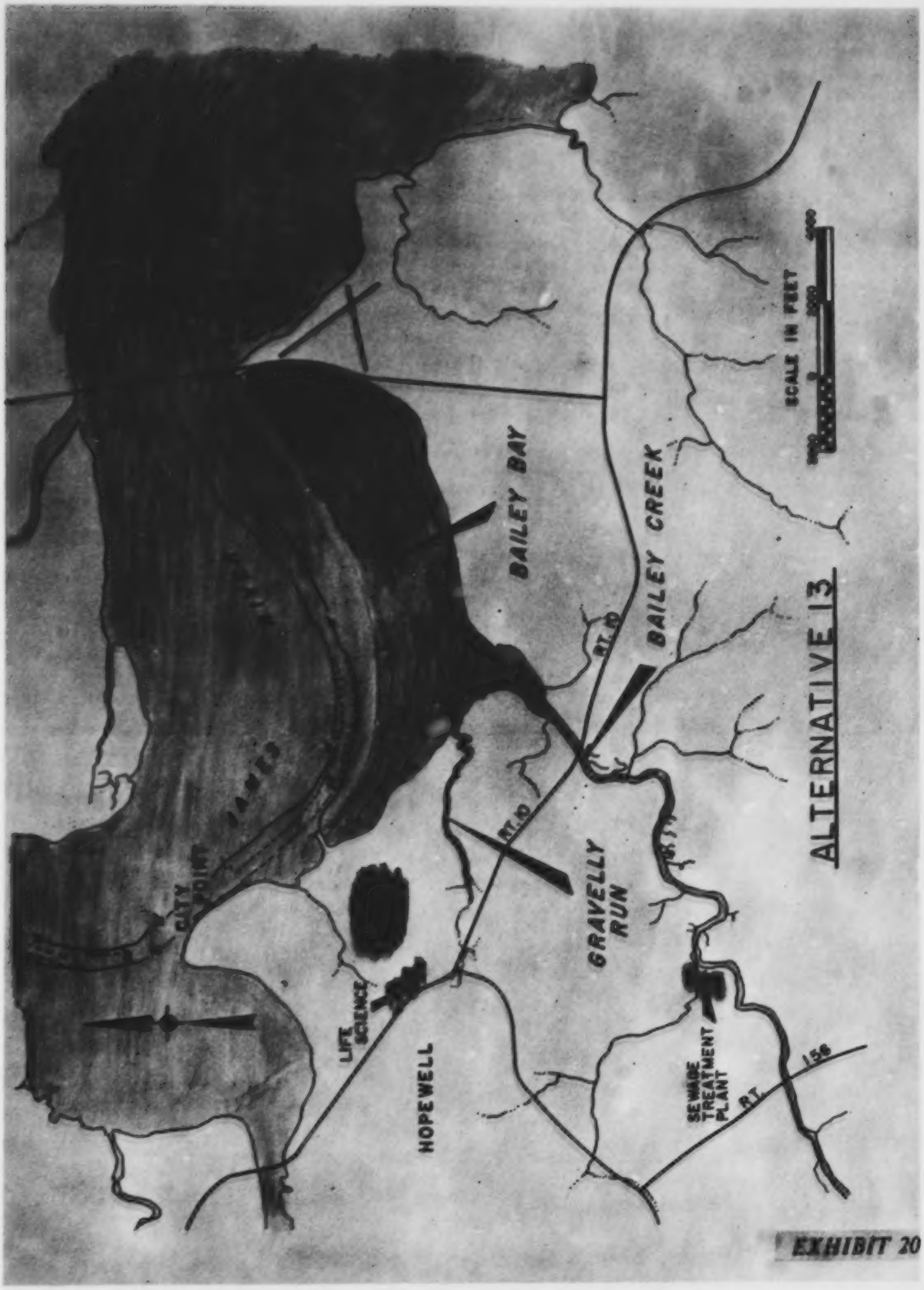
JAMES RIVER
BAILEY BAY
BAILEY CREEK
RT. 10
CITY POINT
GRAVELLY RUN
LIFE SCIENCE
HOPEWELL
SEWAGE TREATMENT PLANT
RT. 156
SCALE IN FEET
1000
0
1000
2000

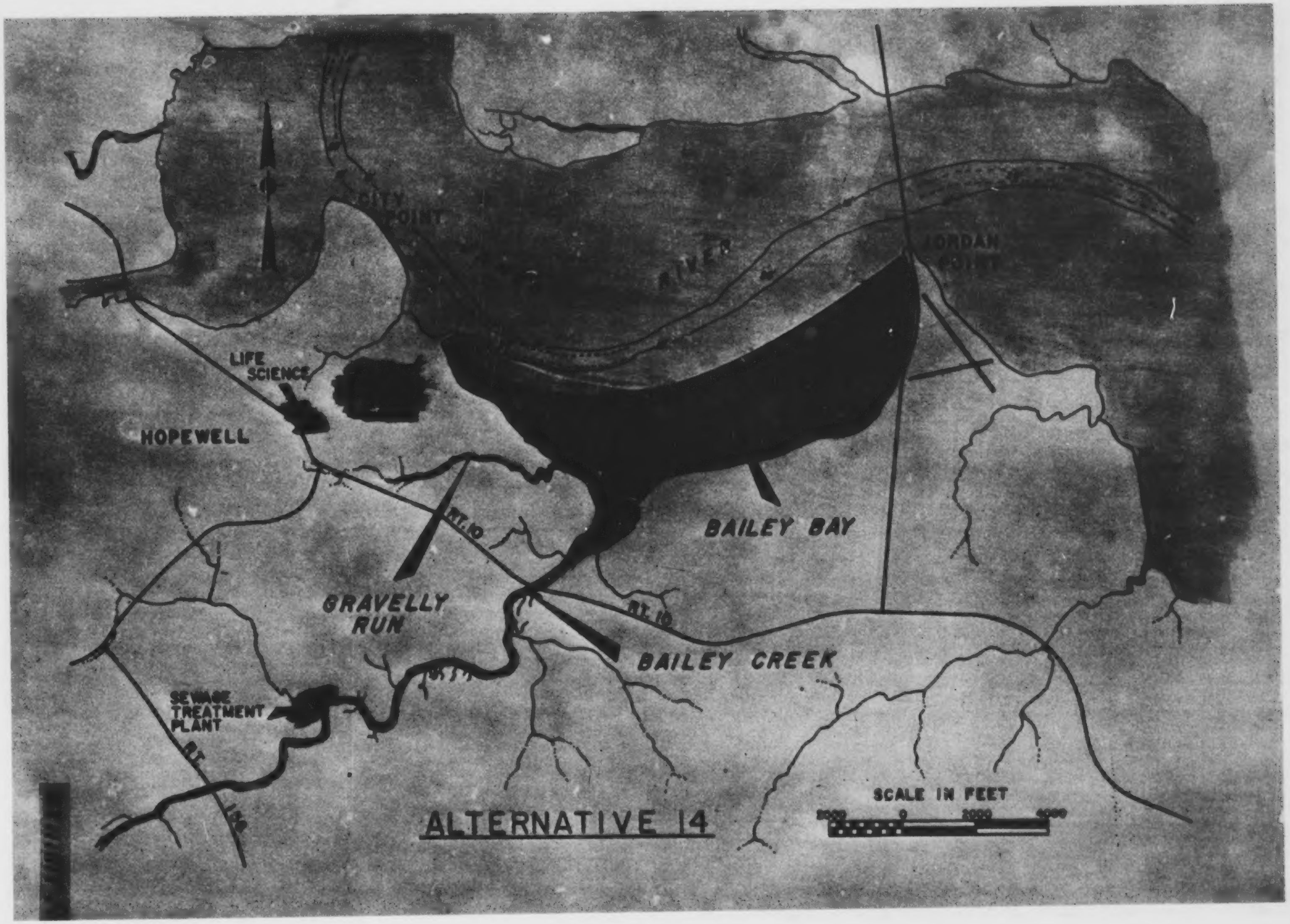
ALTERNATIVE 12A

EXHIBIT 19


CITY POINT
JAMES
BAILEY BAY
BAILEY CREEK
RT. 10
RT. 10
GRAVELLY RUN
LIFE SCIENCE
HOPEWELL
SEWAGE TREATMENT PLANT
RT. 156
SCALE IN FEET

ALTERNATIVE 13

EXHIBIT 20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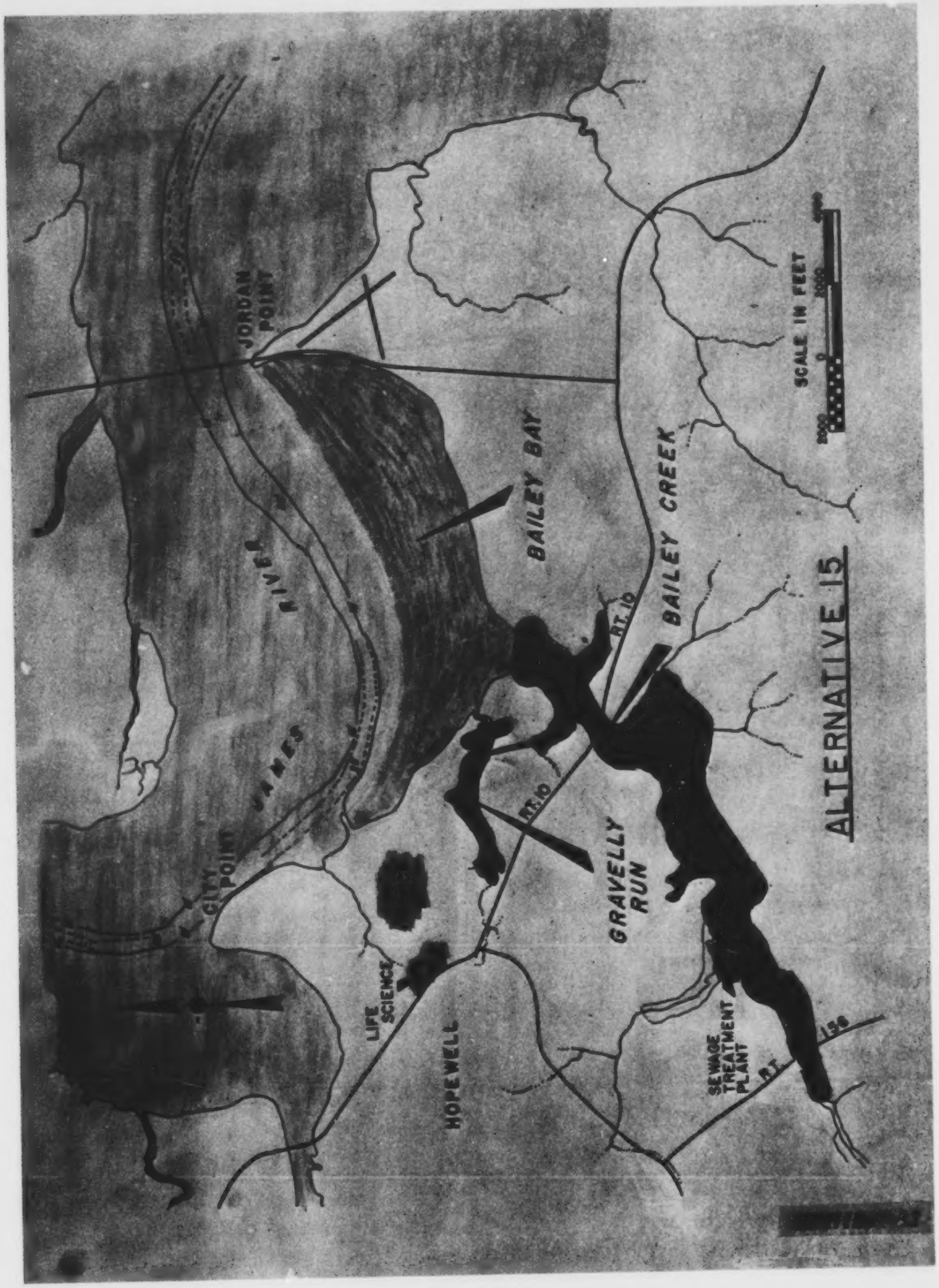
RIVER
JORDAN POINT
LIFE SCIENCE
HOPEWELL
RT. 10
BAILEY BAY
GRAVELLY RUN
RT. 10
BAILEY CREEK
SEWAGE TREATMENT PLANT
RT. 156
ALTERNATIVE 14
SCALE IN FEET
2000
0
2000
4000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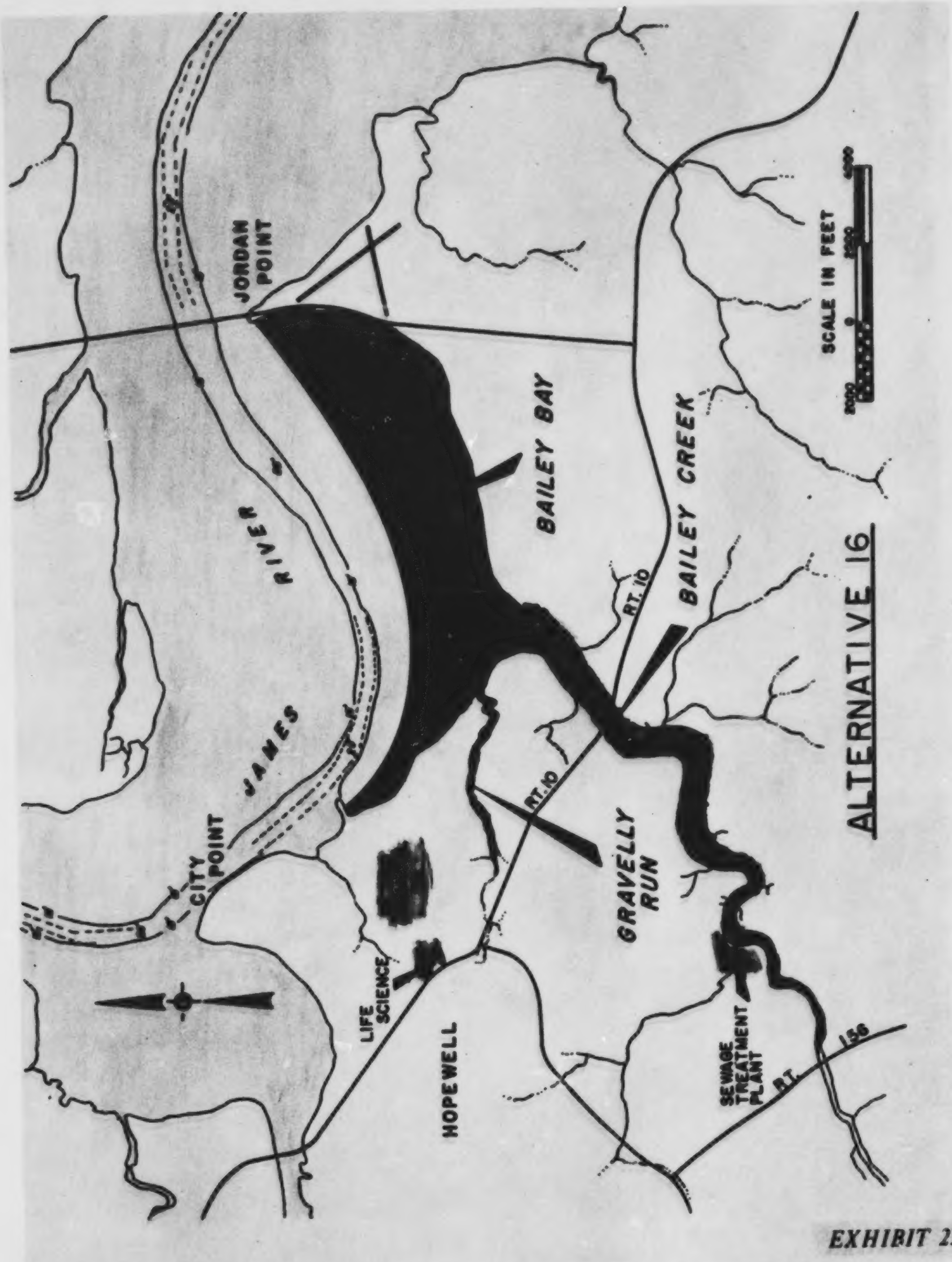
BAILEY BAY
BAILEY CREEK
JAMES RIVER
CITY POINT
GRAVELLY RUN
RT. 10
RT. 10
RT. 10
LIFE SCIENCE
HOPEWELL
SEWAGE TREATMENT PLANT
RT. 156
SCALE IN FEET
2000
0
2000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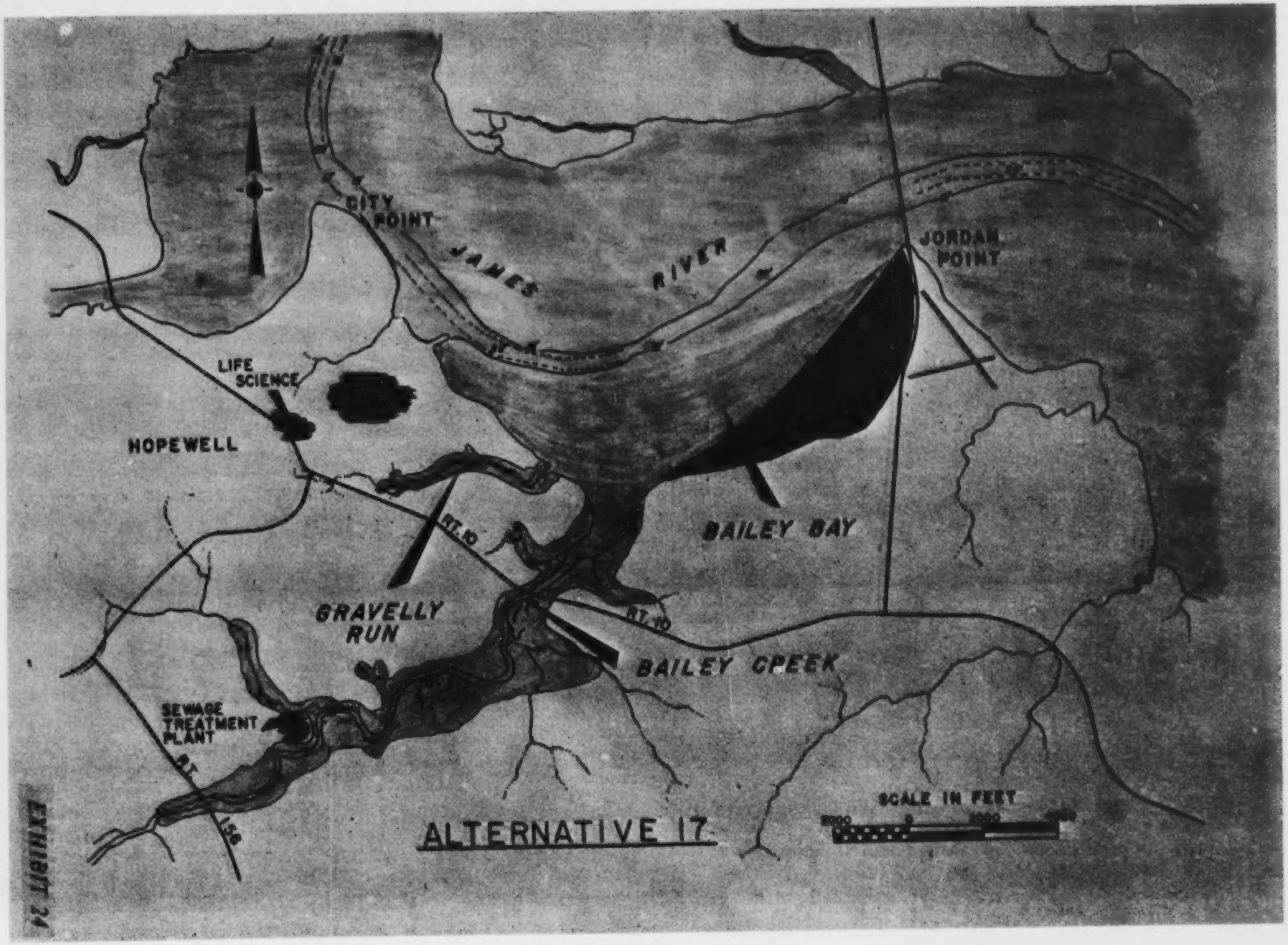
JORDAN POINT
CITY POINT
BAILEY BAY
BAILEY CREEK
RT. 10
RT. 10
GRAVELLY RUN
LIFE SCIENCE
HOPEWELL
SEWAGE TREATMENT PLANT
RT. 156
SCALE IN FEET
2000
0
2000
4000

EXHIBIT 23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JAMES RIVER
JORDAN POINT
LIFE SCIENCE
HOPEWELL
BAILEY BAY
RT. 10
RT. 10
GRAVELLY RUN
BAILEY CREEK
SEWAGE TREATMENT PLANT
RT. 156
SCALE IN FEET
2000
0
2000
4000

ALTERNATIVE 17

EXHIBIT 24

ENVIRONMENTAL ASSESSMENT OF ENGINEERING ALTERNATIVES FOR CAPTURING, STABILIZING, OR REMOVING KEPONE IN GRAVELLY RUN, BAILEY BAY, AND BAILEY CREEK

By

James D. Haluska
U.S. Army Corps of Engineers
Norfolk, Virginia 23510

INTRODUCTION

Concurrent with the engineering study of methods to control the continued leaching and runoff of Kepone contaminated water and sediment from the Hopewell, Virginia area, the Corps conducted an environmental assessment of the impact these proposed measures would have on the Bailey Creek, Bailey, Bay, Gravelly Run, and associated James River ecosystems. The assessment required the survey scale determination of the relative quality of the air, water, sediment, and biological systems of the project area. In addition to these surveys, an inventory of the habitat types present in the project area was conducted by the U.S. Fish and Wildlife Service (FWS) using aerial photography coupled with ground truth data acquisition. After the Corps and FWS scientists had acquired sufficient data concerning the environmental background of the area, an analysis of the environmental impacts of the various alternatives on the project area was performed.

ENVIRONMENTAL INVENTORY COLLECTION

In addition to field surveys and ground truth collection surveys by Corps and U.S. Fish and Wildlife Service personnel, literature searches for data concerning several of the parameters were conducted.

The study area used for this assessment included the drainage areas of Bailey Bay and Gravelly Run, and the Bailey Bay out to James River navigation channel.

Hopewell is an old Virginia settlement dating from 1613. Industrialization of the area began in 1913 and has continued. The history of Hopewell is summarized in the following table.

SUMMARY OF PROJECT AREA HISTORY

Date	Event
1613	Settlement at City Point, called Charles City.
1622	Charles City destroyed by indians. Town rebuilt as Charles City Point.
1635	Charles Eppes receives grant from King Charles.
177?	Benedict Arnold shells Appomattox Manor.
1864-65	Grant headquarters at Appomattox Manor.
1913	Dupont De Nemours Dynamite Plant. Hopewell population estimated at 40,000.
1916	Hopewell incorporated as a city.
1920	Hopewell population 1320.
1920	Samscott Company locates in Hopewell.
1923	Samscott Company becomes Virginia Cellulose Company.
1926	Virginia Cellulose becomes Hercules Powder Company
192?	Tubize Artificial Silk Company, Hopewell China Company, Hopewell Trunk and Bag Company
1928	Atmospheric Nitrogen Corporation
1954	National Analine Division of Allied Chemical fiber operation.
1960	Allied Chemical expansion. Firestone located in Hopewell.

SUMMARY OF PROJECT AREA HISTORY
(Continued)

Date	Event
1974	Life Science Products began operations.
1975	Life Science Products closed.

Data describing the population make up of the Hopewell area have also been collected and estimates of the growth of the area have been made using Tayloe Murphy Institute projections. The current estimate of the area's population is 23,000 people for the city of Hopewell and 18,700 people for Prince George County. A description of the overall social background of the area has been constructed.

Land-use patterns in the area indicate that much of the project area which may be impacted by the alternatives is zoned industrial. The zoning of the Prince George County portion of this same area is residential, but due to steep grades, little development has occurred in the county along the Bay and Creek.

The historical and archeological resources of the area were also researched. Three nearby areas are on the National Register of Historic Places. Five archeological sites are located along the county shore of Bailey Bay and Bailey Creek according to the Virginia Historic Landmarks Commission.

Air and Water quality in the project area has suffered somewhat from the heavy industry on the creek. Three violations of the suspended particulate (NAAQS) standard were rated in the year ending March 1977. Interpretation of water quality data indicates that the lower reach of Bailey Creek has problems caused by effluents which occur in that reach. The water quality picture is complicated by the start-up of a Regional Sewage Treatment Plant near the end of 1977 which presumably will treat the effluents from the industry sited there. Residual effects from the polluted creek sediments are expected to last many years beyond start-up.

The analysis of bottom sediments from the project area was also conducted. The only chlorinated pesticide found was Kepone when a chlorinated pesticide scan and a check for PCB's was done.

The concentrations of several heavy metals indicated that the sediments had been altered by the adjacent industrialization. This ws also indicated by high concentrations of COD, TKN, and organic sulfides in some of the samples.

The habitat typing of the project area employing aerial photography and intensive ground thruth data collection indicated that the wetlands in the project area fall into two main catagories. According to the preliminary results of this analysis, there are 27.0 hectares (66.5 acres) of cattail-amaranthus marsh in the study area, and 106 hectares (263 acres) of type seven wooded swamp in the area. During the field portion of this study, indications were that several of the energy web segments that this type of system should support, were absent. If this is true, this would lend more evidence to the argument that the system is severely stressed.

IMPACT ASSESSMENT

In the final assessment of the proposed alternatives, an environmental scenerio will be qualitatively presented. This scenario, as well as, the other background information will then be used to evalute the impacts of the eighteen alternatives. In addition to the impacts on the natural environment, the alternatives will also be evaluated for their impacts on human activities in the project area.

As of this writing, the environmental impact analysis is not complete and is not being reported at this time.

As a final section of the environmental analysis, a "no action" or "without" projection will be made for the project area and the adjacent James River area. The impact of Kepone contamination on this "extra" alternative will be added by the Environmental Protection Agency after the Corps report is submitted as it will for the other eighteen alternatives.

POTENTIAL DREDGING TECHNOLOGY ON THE WORLD MARKET

BY

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U.S. ARMY CORPS OF ENGINEERS
NORFOLK, VIRGINIA 23510

INTRODUCTION

The Norfolk District, Corps of Engineers, has been requested by the Environmental Protection Agency to evaluate all potential dredging technology on the world market, as well as methods to reduce and control resuspension of concomitant secondary pollution. In this evaluation, a review was made of the dredging technology in the United States, Europe, and Japan, incorporating the mechanical, hydraulic, and pneumatic dredges. Also, methods were investigated to reduce resuspension of sediments.

DREDGING TECHNOLOGY IN THE UNITED STATES

Cutterhead Pipeline Dredge. This dredge is a highly developed machine that is used throughout the world. It is suitable for all but very hard material. A rotary cutter on the end of a dredge ladder bites into and scarifies the bottom material. Then a centrifugal pump sucks water and the suspended material through a pipeline, floated on pontoons, to a disposal site. The diameter of the pump discharge in pipeline dredges varies from 6 to 42 inches. The required draft varies from as little as 2 feet to 12 or 15 feet. The production rate depends on the material to be dredged and the pumping distance. Some of the smaller cutterhead pipeline dredges can dredge 100 cubic yards per hour in mud and soft clays, whereas the large dredges can dredge as much as 2,000 cubic yards per hour. The dredge is generally controlled on stern-mounted spuds and is swung from one side of the channel to the other by swing gear. By the nature of this device, considerable agitation and disturbance of the bottom sediments occur.

Suction Pipeline Dredge. This is similar to the previously described dredge, excluding a cutterhead. This type of machine is used in soft or free-flowing material and sucks the material and dilution water from the channel bottom. It then discharges the mixture through a stern-connected pipeline to a disposal area.

Dustpan Hydraulic Dredge. This is a variation of the suction pipeline dredge and is especially adapted to remove sandbars and alluvial deposits such as sand, silt, mud, and loose gravel from the navigation channels of the Mississippi, Missouri, and Ohio Rivers. Its wide suction inlet is similar in configuration to a vacuum cleaner. Powerful, high-pressure water jets located along the length of the dustpan head are used to scarify the material from the bottom of the river. It is then picked up by the wide but shallow suction opening, pumped through the discharge line, and then returned into the water adjacent to the dredge.

Hopper Hydraulic Dredge. This dredge is equipped with hoppers that store the hydraulically dredged material until it is carried to a place of disposal. It is equipped with large centrifugal pumps similar to those employed by suction dredges. The suction pipes are hinged on each side of the ship with the intake or drag arm toward the stern of the vessel. The head is dragged along the bed of the area to be dredged as the vessel moves forward. The dredged material is lifted up the suction pipe and stored in the hoppers of the ship. The hopper dredge is highly mobile and, unlike the pipeline dredges previously described, has no attached pipeline. Dredging is at times continued to the point where the hoppers start to overflow and the excess water containing fine materials is allowed to flow back into the water body. Disposal can take place in the ocean by opening the bottom of the hoppers or the dredge can tie up to a dock and pump dredged material directly ashore into a disposal area.

Sidecasting Dredge. This dredge is a relatively new development and one particularly effective where the littoral currents do not retain a significant amount of dredged material in the navigation channel. The material is picked up with dilution water by the draghead sliding over the bottom. It flows through suction piping and a centrifugal pump before being pumped back into the waterway, through pipes ranging from 70 to 100 feet in length.

Dragline Mechanical Dredge. This dredge resembles an ordinary metal scoop suspended from a swinging boom on a crane that is mounted either on a barge or truck. The scoop is lowered into the material to be excavated and is then placed in such a position as to slice the earth away as the scoop is drawn towards the crane. When the scoop is filled, it is lifted and the dredged material is deposited either in a barge or on the bank. Considerable turbidity is created during the operation.

Dipper Mechanical Dredge. This dredge includes a single shovel generally mounted on a floating dredge, caterpillar, or crawling tractor. The shovel is firmly attached to a long boom and is forced into the material to be dredged and the material is scooped up. The shovel is then lifted and the dredged material is deposited either in a barge, truck, or other conveyance or on the bank.

Grab Bucket Dredge. This dredge consists of a self-filling bucket suspended from a swinging boom or crane. It is often called a clamshell dredge when there are two halves to the bucket. Material is removed by forcing the opposing bucket edges into it while the dredge or truck on which it is mounted is stationary. The bucket is then lifted and the dredged material is deposited either in a barge or other conveyance, or on the bank.

Endless Chain Dredge. This dredge consists of a continuous or endless chain of buckets pulled around a dredging ladder. Material is removed by forcing the single cutting edge of successive buckets into the material. The dredge lifts the buckets and deposits the dredged material in a barge, conveyor belt, or other conveyance.

Mud Cat. This dredge has the capability to operate in about 27 inches of water. It is small and equipped with a horizontal, auger-type, cutterhead attached to a hydraulic boom at the front end of the dredge. A mud shield surrounds the auger and helps pull the material to the pump suction intake and reduce resuspension. It can discharge approximately 1,500 gallons per minute of slurry with a solids concentration of 10 to 30 percent. This varies from 45 to 135 cubic yards of solids per hour. Generally, the Mud Cat dredges more efficiently during a backward cut than during a forward cut. This is true from both a solids removal and a sediment resuspension aspect. During a backward cut, the mud shield is lowered over the auger, and the bottom sediment is dragged into the auger.

Silt Curtains. Silt curtains, turbidity barriers, or "diapers" as they are sometimes referred to, can be used to surround dredging or disposal operations as a means of containing or controlling the dispersion of turbid water created by the operation.

DREDGING TECHNOLOGY IN CANADA

Canada uses dredges similar to those used in the United States. They include such hydraulic dredges as the cutterhead and suction pipeline, as well as hopper dredges.

DREDGING TECHNOLOGY IN EUROPE

Pneuma Dredge. The Pneumatic International S.A. of Italy has developed a new system operated by compressed air, for dredging sand, gravel, mud, silt, or clay. It includes three steel cylinders usually of the same section and height. At the bottom of each cylinder is one entrance pipe for the mixture; at the top is a pipe for the introduction and release of compressed air and a second pipe for removing the mixture. The latter pipe extends almost to the bottom of the cylinder. In each cylinder there is a valve above the entrance pipe. Each cylinder is filled with a mixture of water and silt, sand, mud, etc., by a counter pressure due to the hydrostatic head when the pneuma cylinders are immersed in water. As soon as one cylinder is filled, the inlet valve automatically closes by its own weight. When a cylinder has been filled, compressed air, supplied by a compressor through the distributor and air hose, acts as a piston and forces the mixture to be expelled from the cylinder to the delivery pipes. some of the advantages of the Pneuma system follow:

a. Continuous and uniform flow.

b. Practically no wear since there are no mechanisms in contact with the abrasive mixture except for the self-acting spherical rubber valves.

c. Percentage of solids up to 60 to 80 percent in volume.

d. Particularly suited for dredging polluted materials since it does not disturb the bed while dredging and therefore avoids secondary pollution.

e. Can be readily dismantled for transport over highways.

Pressair Sand-Pump Dredge. A German company has developed dredging equipment that is operated by compressed air. Through the outer shell of a double tube, compressed air is forced into the suction pressure head which is positioned on the bottom of the water. In the suction pressure head, air is forced through a nozzle pipe into the lower part of the suction head. The hydrostatic pressure at this point then becomes less than the pressure of the surrounding water, resulting in an upward suction which conveys the material to be dredged and the water to the surface. This dredge is capable of dredging to depths of 262 feet.

IHC Amphidredges. A series of small dredging units have been added to the range by IHC Holland. They are designed for dredging under wet or marshy site conditions. They can be transported by truck or trailer. They include three kinds of dredging techniques--clamshell grab dredging, backhoe dredging, (operates like a dragline), and cutter suction dredging.

DREDGING TECHNOLOGY IN JAPAN

In recent years, Japan has achieved rapid economic progress. However, the environment surrounding the manufacturing enterprises has deteriorated to a marked extent. Waste water from factories and industrial wastes have produced sludge that has contaminated the sea.

Toxic substances present in the sludge have destroyed the environment, and local fishermen have been obliged to change or abandon their occupation. Settling of the sludge also hindered the passage of ships. Thus, the social problem became serious. Accordingly, the Japanese have undoubtedly concentrated on improving the dredging technology for avoiding resuspension of sediments more than any other country in the world.

Clean Up Hydraulic Dredge. The dredge itself looks like a conventional hydraulic cutterhead except for the clean up head installed on the ladder. It is equipped with a moveable wing or shield in front of the equipment so as to overlie the bottom sediments. It has a moveable shutting plate which intercepts the flow of outer water, and a mixing device, somewhat like an auger, contained in the equipment that moves material to the suction pipe.

Anti-Turbidity System for Hopper Dredges. In dredging operations excess water from the hopper ben is discharged overboard above the water line. As a result, surrounding waters are made turbid by the excess water mixed with material, and currents and winds spread the turbidity over wide areas. The anti-turbidity system consists of baffles and the overflow is discharged below the water line.

Oozer Pump. It is a pneuma system which can dredge in very shallow water. Usually two tanks are used as front attachments, to increase operating efficiency. Sludge is pumped up continuously as the two tanks perform the suction and discharge processes alternately. As a vacuum plus water pressure is created inside the tank, the sludge pushes up the conical suction valve and flows into the tank. The vacuum pump is not needed when the operation is carried out at a depth where water pressure alone provides a sufficient suction force. When sludge has risen to the level of the upper sensor rod, the sludge suction cycle terminates. Atmospheric air is delivered into the tank. The compressed air is sent in by the compressor. This pressure in the tank causes sludge to push up the ball valve at the outlet and to be discharged.

Pressure Releasing Process. Upon completion of the suction and discharge processes, residual pressure inside the tank is released into the air. Then the operation is repeated.

Water-Tight Grab Bucket. The bucket is of the closed type, especially designed for dredging without giving rise to secondary pollution when it is used for dredging settled sludge. The company has developed a dredging type bucket for use in shallow sedimented layers. The bucket for handling soft mud, dredges the sludge without giving rise to secondary pollution as a result of its design and shape.

REMARKS

This paper covers various dredging equipment utilized throughout the world. Any dredging activity must not only consider the dredging equipment involved, but the conveyance as well as the disposal area. This should be considered as a total and integrated system and not as separate components.

SESSION IIB

"Kepone Feasibility Study - Battelle Northwest"

CHAIRMAN

Mr. Kenneth M. Mackenthun
Director
Criteria and Standards Division
Office of Water and Hazardous Materials
U.S. Environmental Protection Agency

SPEAKERS

Mr. Steven J. Shupe
Battelle Northwest Laboratories
"Current Deposition of Kepone Residuals in the Hopewell, Virginia Area"

Dr. Yasuo Onishi
Senior Research Scientist
Battelle Northwest Laboratories
"Mathematical Simulation of Transport of Kepone and Kepone-Laden Sediments in the James River Estuary"

Gaynor W. Dawson
Manager, Water and Waste Management
Battelle Northwest Laboratories
"Preliminary Evaluation of Approaches to the Amelioration of Kepone Contamination"

CURRENT DEPOSITION OF KEPONE RESIDUALS IN THE HOPEWELL, VIRGINIA AREA[a]

by

Steven J. Shupe
Gaynor W. Dawson

BATTELLE
Pacific Northwest Laboratories
Richland, Washington 99352

(a) Publication of this paper requires final Battelle approval pending ERDA clearance.

CURRENT DEPOSITION OF KEPONE RESIDUALS IN THE HOPEWELL, VIRGINIA AREA

by

Steven J. Shupe
Gaynor W. Dawson
Battelle, Pacific Northwest Laboratories
Richland, Washington

BACKGROUND

In April 1977 Battelle, Pacific Northwest Laboratories initiated a study with the Environmental Protection Agency to undertake the first phase of an effort to determine the feasibility of removing kepone from the James River. One aspect of this research involved a field sampling program designed to establish the extent of kepone deposition in and around the City of Hopewell, Virginia. Emphasis was placed on identifying specific areas of high kepone concentration which could potentially serve as continuing sources of contamination to the James River system.

This paper presents a summary of the data collected over the past five months of the sampling program. With additional samples and results remaining to be analyzed as part of Battelle's overall kepone deposition investigation, it is premature at this time to discuss concrete conclusions resulting from this study. Therefore, this paper focuses on presenting the data collected and not on interpreting these data to any significant degree. The conclusions and recommendations of this research program will be incorporated in the report to be submitted to the Environmental Protection Agency by Battelle in November of this year.

Study Area

The exact amount of kepone released into the environment since production began in Hopewell in 1966 is not known. It has been estimated, however, that roughly one hundred thousand pounds of the chemical were released during the period 1966 to 1975 from the Allied Chemical Corporation semi-works plant and the Life Sciences Products Company. This total resulted from the continuous release of kepone-saturated wastewaters, particulate emissions, and bulk disposal of waste batches of the chemical.

Figure 1 shows the location of the two plants that produced kepone in Hopewell. The Life Sciences plant began operating following the cessation of Allied's kepone production in 1974. Also located on this figure are features relevant to the design of the kepone field sampling program. These include:

- the City of Hopewell's sewage treatment plant which received the liquid waste from the Life Sciences operations
- the City's landfill area where waste kepone was dumped as well as sewage sludge contaminated with the chemical
- the Kepone Lagoon adjacent to the sewage treatment plant which contains kepone-contaminated sludge
- Bailey Creek into which the treated sewage effluent flows, as does much of the runoff from the landfill
- Cattail Creek which also receives some of the landfill runoff
- Gravelly Run which received the effluent from Allied's kepone production facilities

Also pictured in Figure 1 is Bailey Bay, a subtidal flat of the James River where high levels of kepone were found in previous testing. It was suspected that the Bay acts as an intermediate, or perhaps ultimate, sink

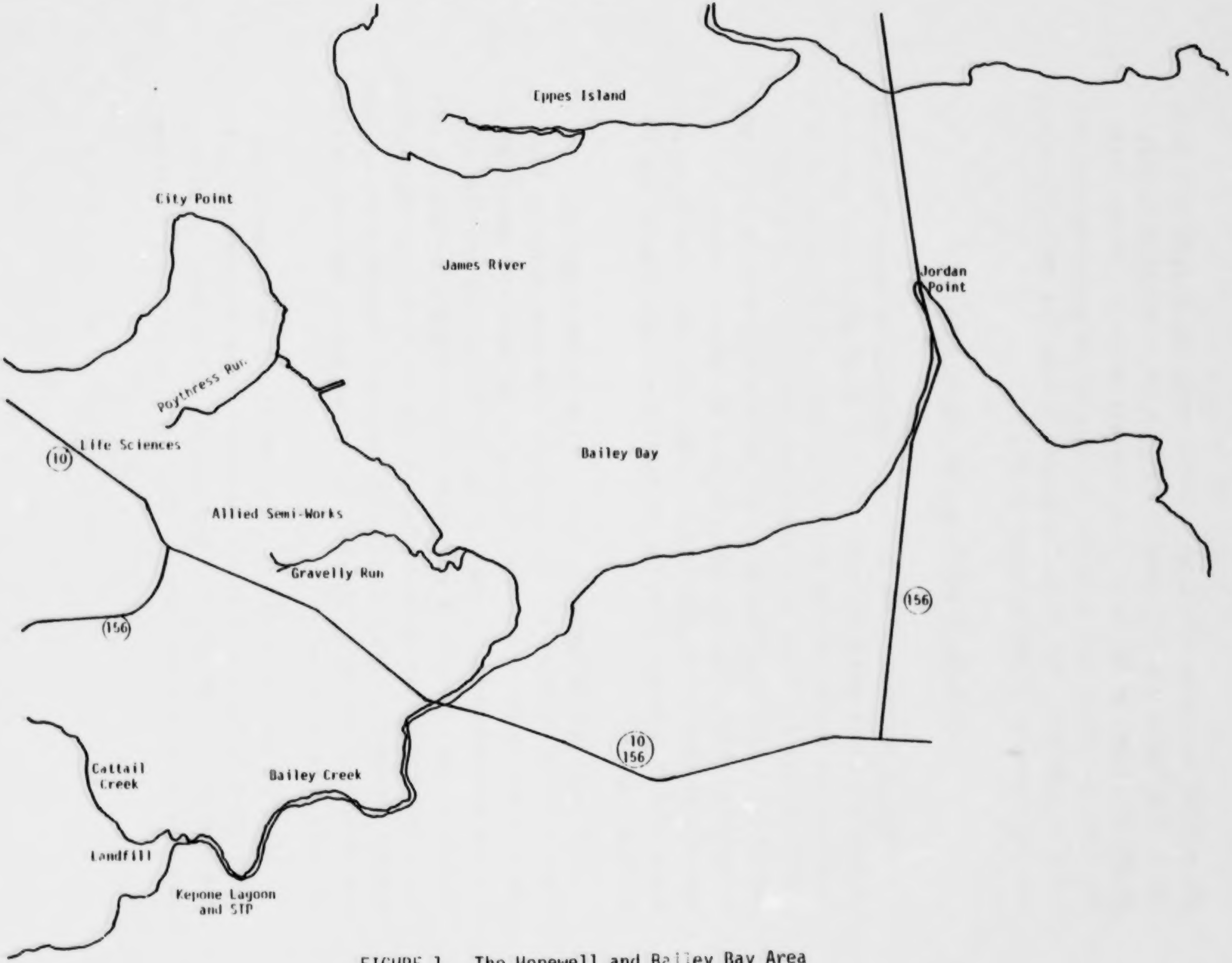

Eppes Island
City Point
James River
Jordan Point
Poythress Run
Life Sciences
(10)
Bailey Bay
Allied Semi-Works
Gravelly Run
(156)
(156)
(10)
(156)
Cattail Creek
Bailey Creek
Landfill
Kepone Lagoon and STP

FIGURE 1. The Hopewell and Bailey Bay Area

for much of the kepone discharged. Consequently, one of Battelle's first goals in designing the field sampling program was to establish to what extent this might be the case. Also, the data resulting from the Bailey Bay sampling will be used as an aid in designing and evaluating alternate clean-up proposals. The methodologies used in this task and the resulting data are presented in the following section.

SAMPLING IN BAILEY BAY AND ITS TRIBUTARIES

The main component of the Bailey Bay sampling program was the collection of core samples of bottom sediment. In order to establish core sampling locations, the Bay was divided graphically into a grid of spaces 1000 ft by 1000 ft (Figure 2). Every other square was selected in a checkerboard fashion for coring, resulting in a total of 28 core samples in Bailey Bay. In addition, three cores were collected from the western crescent of Tar Bar immediately downriver of Jordan Point. Also, cores were taken at approximately 2000 ft intervals along the aforementioned creeks flowing into the Bay from Hopewell.

All cores were collected in 33-in. long cellulose acetyl butylrate tubes, 2 1/8-in. in diameter. In conditions where water depth was less than 1 ft and the bottom was relatively soft, the tubes were penetrated into the sediment directly, capped on top for suction, and extracted with the core inside. However, in most cases it was necessary to place the tube into a coring apparatus for collecting the sample. A stainless steel cutting head was used on the tip of the corer to facilitate penetration and extenders were attached to the top of the corer jacket that encased the tubes to allow for sampling in deeper water.

After the cores were collected they were frozen and shipped to the laboratory at Battelle in Richland, Washington. Here they were analyzed to determine the concentration of kepone within the sediment. Initially, cores from seven selected locations (Figure 3) were cut into 1 and 2-inch

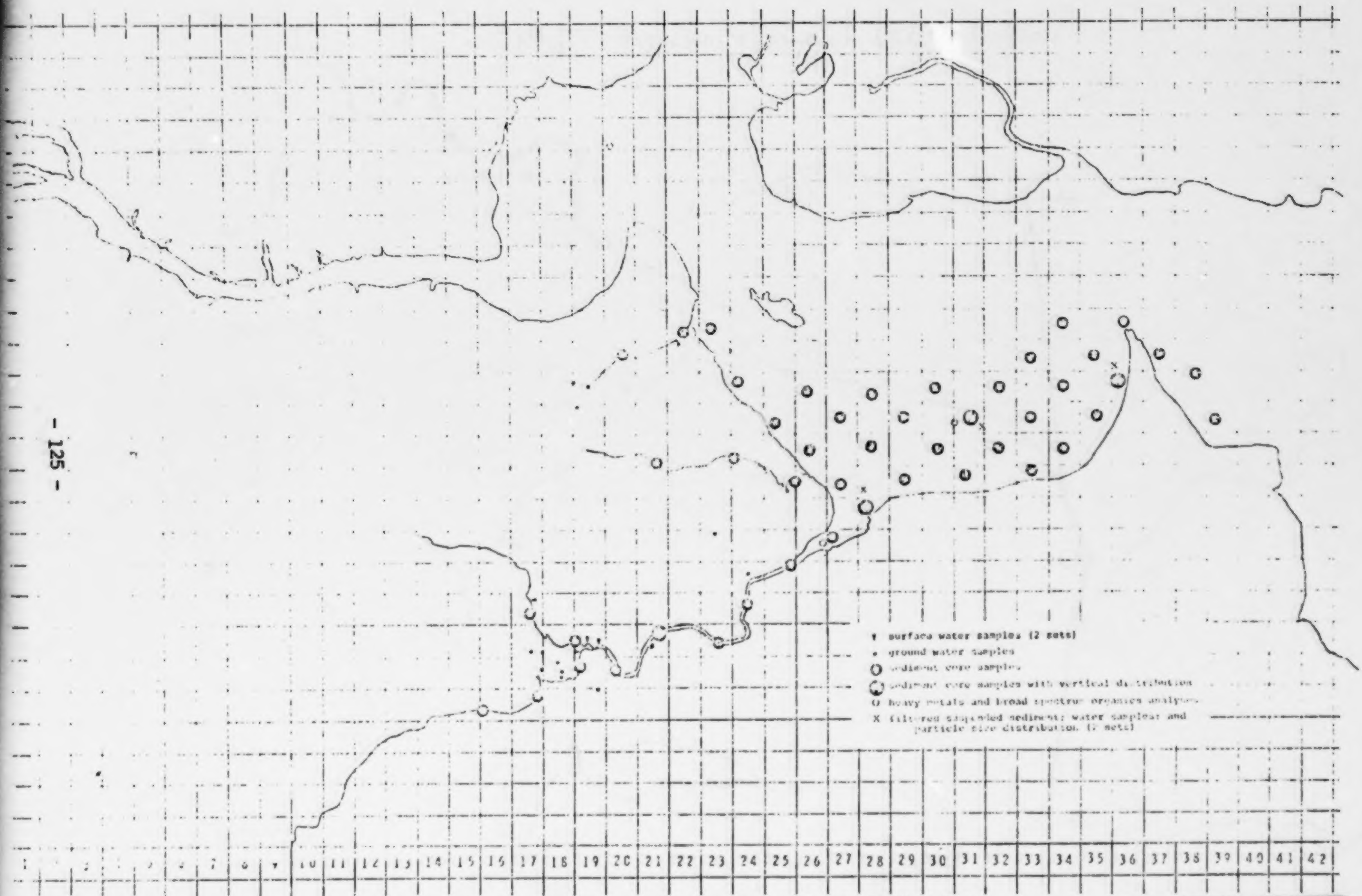

surface water samples (2 sets)
ground water samples
sediment core samples
sediment core samples with vertical distribution
heavy metals and broad spectrum organics analyses
X filtered suspended sediment; water samples; and particle size distribution (2 sets)
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42

FIGURE 2. Sampling Grid for Hopewell and Bailey Bay

Reproduced from best available copy.

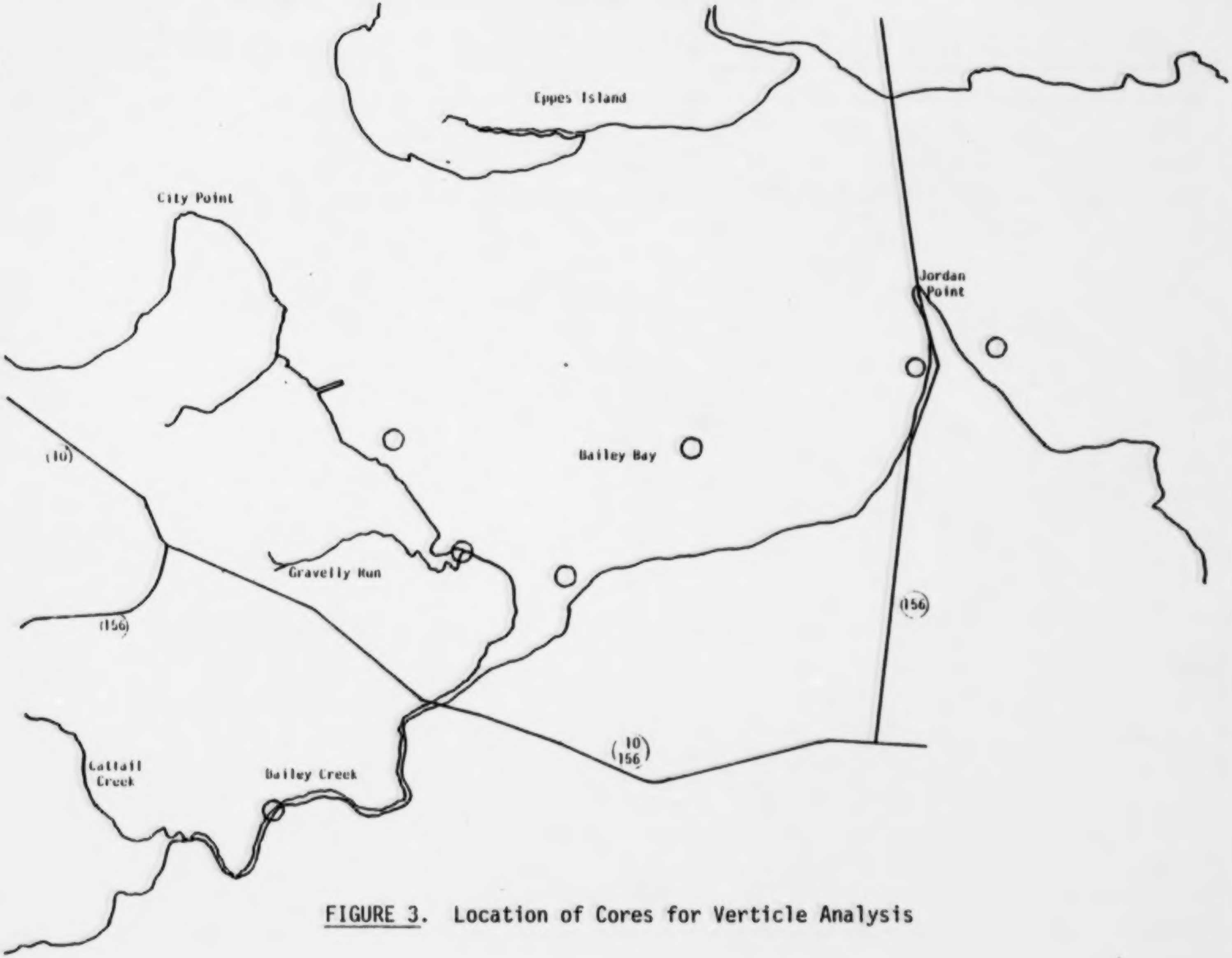

Eppes Island
City Point
Jordan Point
Bailey Bay
(10)
Gravelly Run
(156)
(156)
(10 156)
Cattail Creek
Bailey Creek

FIGURE 3. Location of Cores for Verticle Analysis

sections and analyzed for kepone in order to detect any vertical distribution patterns that might exist. The resulting data (Table 1) provide not only an informative picture of kepone distribution, but also a guide to establishing the standard depth to which the remaining cores should be cut before individually mixing each of them into a homogenized sample. The selected standard length of core extends from its upper surface down to a depth of 12 in. Figure 4 presents the results of kepone detection analyses of these homogenized core samples.

The homogenized cores show a definite pattern of deposition corresponding to known flow paths for Bailey's Creek water. The predominant direction of that flow is along the eastern shore and across Jordan Point with back eddying into western Tar Bay. Under some conditions, a strong incoming tide will reverse this flow and bring it up the western shore along City Point. The western shore is also exposed to contributions from Gravelly Run and Poythress Run.

The vertical core analysis reveals that the more highly contaminated sediments (Bailey Creek, mouth of Bailey Creek, western shore between Poythress and Gravelly Run outlets, and Jordan Point) are distributed in a bell-like configuration with depth. That is, concentrations increase from the surface to a depth of 4 to 7 in., and then decrease with further depth. This probably reflects a relatively uniform deposition rate wherein less contaminated sediments are now being deposited over the highly contaminated sediments from the 1974-1975 period.

The less contaminated cores (Tar, Bay, Bailey Bay Midpoint, and Gravelly Run) display a different pattern. These cores show decreasing kepone concentration with depth. This is reflective of low deposition rates. It appears that less active sedimentation caused lower amounts of contaminated particulates to be deposited in these locations in the first place, and current low rates have prevented the older deposits from being completely covered by new, uncontaminated particles.

TABLE 1. Kepone Distribution in Sediment Cores with Depth (ppm)

Depth From Surface (Inches)	Bailey's Creek Above Bridge	Bailey's Creek Mouth	Gravelly Run Mouth [Not Detected]	Midway Poythress and Gravelly Runs	Mid Bay	Bailey Bay Jordan Pt.	Tar Bar Jordan Pt.
1	0.81	1.36	<0.34	0.11	0.19	0.95	1.09
2	0.59	1.66	<0.10	0.13	0.03	0.86	1.27
3	1.30	2.54	<0.05	<0.08	0.03	0.87	0.42
4	0.78	3.88	<0.09	0.15	0.01	0.87	0.03
5	16.46	14.07	<0.09	0.92	0.01	1.25	0.02
6	2.91	40.74	<0.10	0.80	0.03	3.63	<0.01
7	65.14	42.29	<0.06	0.30	<0.01	17.80	<0.01
8	19.17	13.87	<0.06	<0.04	<0.01	0.17	<0.02
9	0.90	4.34		<0.03	<0.01	0.16	<0.01
10	0.45	0.86		<0.03	<0.01	0.14	<0.02
11		<0.51					
12		<0.42					
13		<0.19					
14		<0.10					
15		<0.14					
16		<0.04					

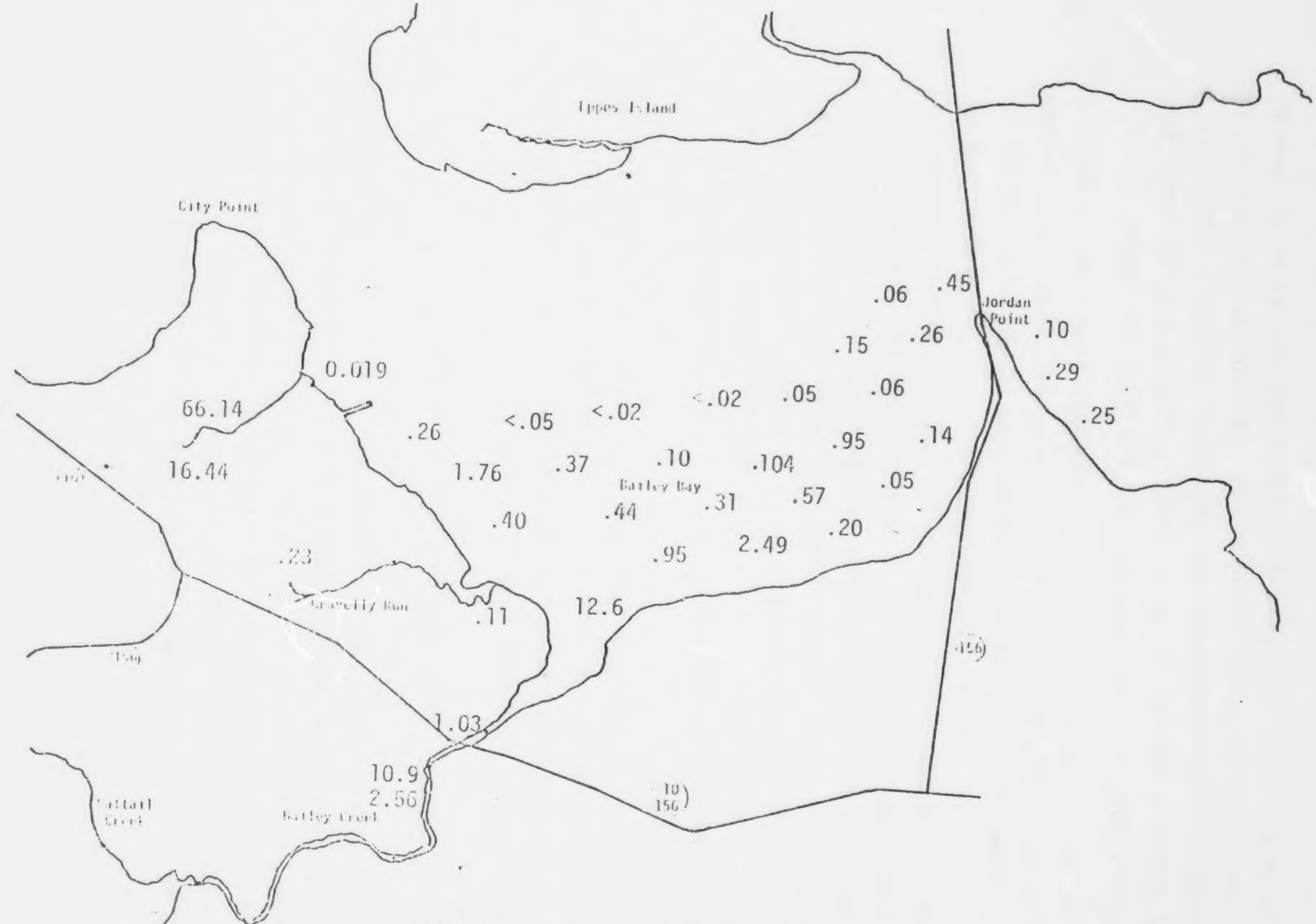

Eppes Island
City Point
Jordan Point
Bailey Bay
Gravelly Run
Bailey Creek
Cattail Creek
10
156
156
.06
.45
.10
.15
.26
.29
.25
0.019
66.14
16.44
.26
<.05
<.02
<.02
.05
.06
.95
.14
1.76
.37
.10
.104
.05
.40
.44
.31
.57
.20
.95
2.49
.23
.11
12.6
1.03
10.9
2.56

FIGURE 4. Results of Kepone Analysis for Homogenized Cores at a Depth of Twelve Inches

The data from the core samples present a good picture of the general deposition pattern of kepone in Bailey Bay. However, further sampling was undertaken in order to determine onto what sized sediment particles the kepone generally adheres. This involved fractioning selected cores into their silt, sand, and clay components and analyzing for kepone.

The cores selected for this latter task were taken from the mouth of Bailey Creek (K-28), Bailey Bay Midpoint (N-31) and Jordan Point (O-36). Table 2 shows the concentration of kepone found in each size fraction of these cores. The sand fraction represents all particles greater than 74 microns in diameter; silt includes particles with diameters between 2 and 74 microns; and clay is composed of particles less than 2 microns in diameter. The highest concentration of kepone was found in the sand fraction in all cases. However, sand constitutes only 18 to 25% of the total bottom sediments in Bailey's Bay. In the three cores taken from different parts of the Bay, silt was the most predominant comprising 47 to 69% of the total sediment; clay accounted for the remaining 13 to 30% of this total.

In the samples analyzed, there was also a trend of increasing kepone concentration with loss on ignition. This combined with the particle size fractionation suggests that in contaminated areas, kepone will be preferentially found on the larger organic particles.

SAMPLING IN THE CITY OF HOPEWELL

Extensive sampling was also undertaken within the City of Hopewell in order to gather clues concerning the extent that atmospheric, hydrologic, chemical, biological, and human transport mechanisms have dispersed the kepone. A variety of samples were collected to determine where significant deposits of the chemical reside and how such deposits might find their way into the James River system. Samples collected include:

TABLE 2. Delineation of Grain Size and Kepone Content in Bailey Bay Sediments

Sample Location	Particle Size	Fraction of Total Sample (%)	Kepone Concentration μg/g (ppm)	Fraction of Total Kepone in Sample (%)
Jordan Point	Silt	48	0.37	11
	Sand	22	5.65	80
	Clay	30	0.47	9
Mid Bay	Silt	47	0.08	35
	Sand	25	0.25	58
	Clay	28	0.03	7
Mouth Bailey Creek	Silt	69	11.74	65
	Sand	18	19.82	29
	Clay	13	5.61	6

- groundwater from wells and springs
- streamflow and rainfall runoff
- soils
- water from the City's sewer lines and sewage treatment plant

Each sample collected was sent back to the Battelle laboratories and analyzed for kepone. The results of these analyses are presented in the following sections.

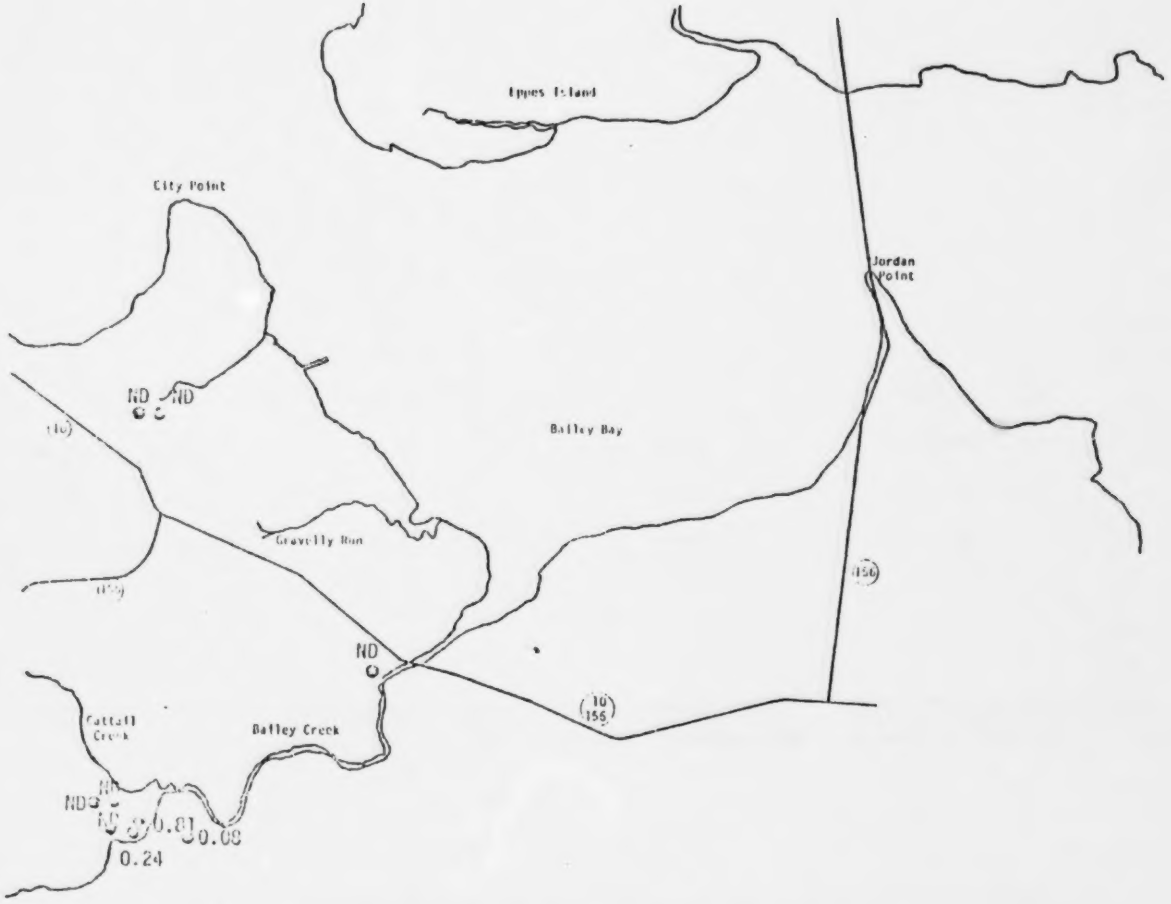
Groundwater

In May of this year samples of groundwater were collected from nine wells in the Hopewell area. The location of these wells are shown in Figure 5. Seven of the wells are maintained by the State Water Control Board as monitoring wells and two are privately owned. The results of the kepone analyses run on these samples showed that most of the water collected had undetectable amounts of the chemical. However, in a few samples kepone was present, with the highest level occurring in State Well #8 used to monitor the Kepone Lagoon.

Groundwater seeps were also discovered flowing from the bank below the area of the Kepone Lagoon into Bailey Creek. These seeps were sampled; the result are presented in Table 3. Note that seep E contains significantly cantly more kepone than any other groundwater sampled. Efforts are currently being made to establish the source of this contamination.

Surface Runoff

Various surface water samples were taken from the streams around Hopewell. Samples were generally collected downstream of suspected areas of contamination as well as from upstream sites to serve as control points. When possible, two samples were taken at each site, one during a dry period and the other shortly after a significant rainfall. The kepone concentrations found in these samples are shown in Figure 6.



Eppes Island
City Point
Jordan Point
Bailey Bay
ND
ND
(10)
Gravelly Run
(156)
(10)
(156)
ND
Cattail
Creek
Bailey Creek
ND
ND
ND
0.81
0.08
0.24

FIGURE 5. Results of Groundwater Analysis May 17-18, 1977 (µg/l-ppb)

TABLE 3. Kepone Levels in the Vicinity of the Disposal Lagoon

Location	Kepone Concentration May 28 (µg/l-ppb)	Kepone Concentration July 8 (µg/l-ppb)	Kepone in Centrate July 8 (µg/l-ppb)	Kepone in Soil July 8 (µg/g-ppm)
A-Puddle in Road	5.28			.17, .09 - Dike high, low
B-Seep Near Creek <0.1 cfs	0.84			.03
C-Moist Patch at Base of Hill	0.20	0.40	.47	
D-Seep at Base, 0.1-0.2 cfs	0.22	<.12	<.17	
E-Seep in Marsh Area, .5 l/sec	17.40	18.38	18.43	3.88
Lagoon	97.50		213	

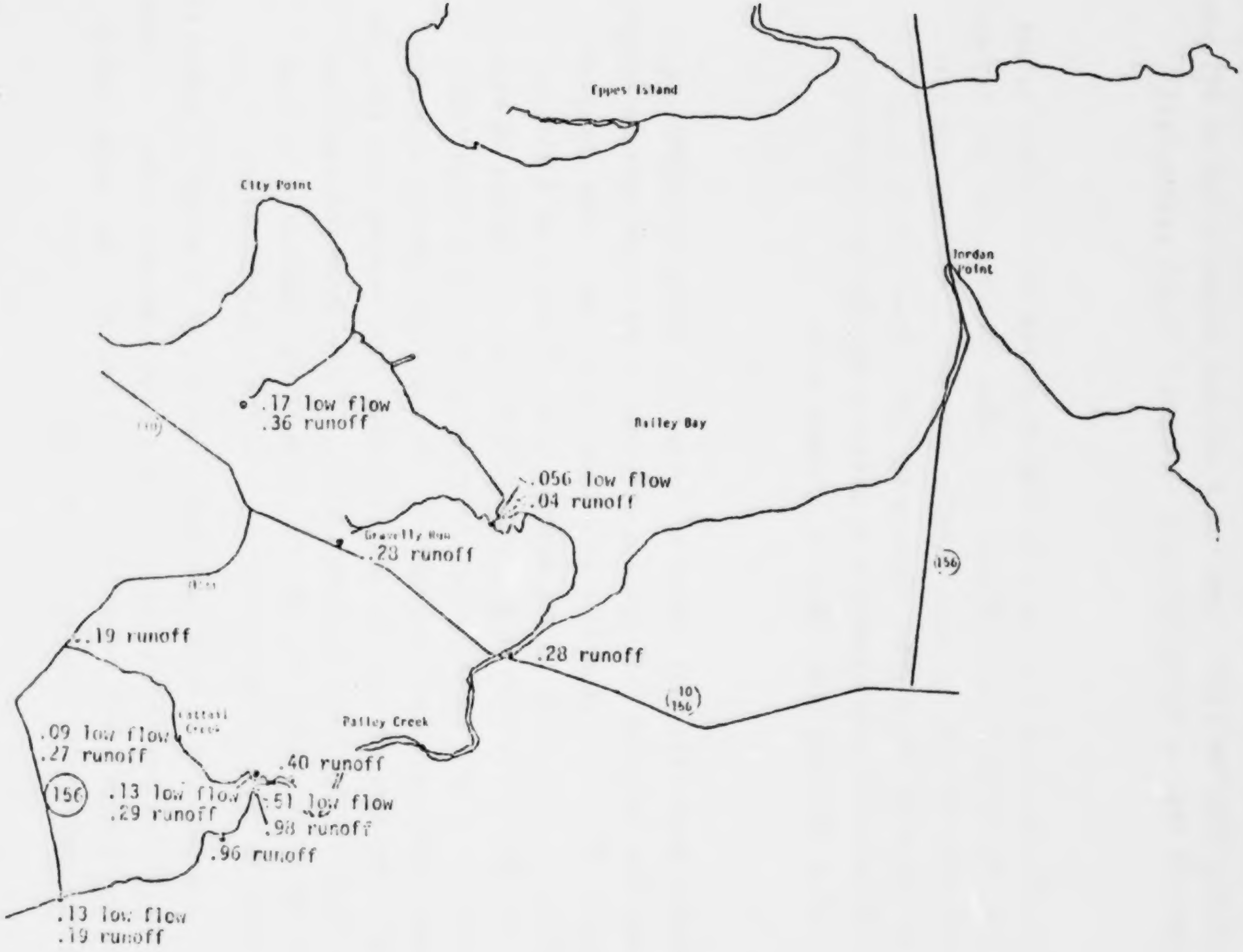

Eppes Island
City Point
Jordan Point
Bailey Bay
.17 low flow
.36 runoff
.056 low flow
.04 runoff
Gravelly Run
.28 runoff
156
.19 runoff
.28 runoff
10
156
Cattail Creek
Bailey Creek
.09 low flow
.27 runoff
.40 runoff
156
.13 low flow
.29 runoff
.51 low flow
.98 runoff
.96 runoff
.13 low flow
.19 runoff

FIGURE 6. Effect of Runoff on Movement of Kepone in Hopewell Area Concentrations in µg/l (ppb)

Without exception, tributary kepone concentrations rose under run-off conditions. Surface water samples were also taken around the Life Sciences site. Water flowing into the sewer lines had a measured concentration of 390 ppb, while overland flow in nearby Nitrogen Park had a 50 ppb kepone level.

Soil

Soil samples taken from the city also displayed their highest values around the Life Sciences site (Figure 7). Note, however, that the highest level detected, 208 ppm, is significantly less than the 20,000 ppm measured shortly after the plant's closure in 1975. Other levels found in soil in the Hopewell area generally displayed a decreasing concentration with increased distance from the Life Sciences site.

Sewage

Samples taken this past summer at Hopewell's sewage treatment plant have shown that both the influent and effluent of the plant contain detectable amounts of kepone, generally at a level of 0.5 ppb. When these concentrations are multiplied by the average sewage flowrate of 3 million gallons per day, it is seen that a significant amount of kepone is associated with the City's sewer system. Further samples were taken from trunk sewer lines, as shown in Figure 8. In addition, samples were collected of slime scraped from the combined sewer line leading from the Life Sciences site to the sewage treatment plant. Forty-three ppm kepone was found in the slime nearest to the site, with levels decreasing to 1 ppm in the slime in the pump station adjacent to the treatment plant.

The data gathered to date have been inconclusive in actually pinpointing the sources of all the kepone reaching the sewage treatment plant. An integrated investigation involving additional soil, runoff, and sewage samples is currently underway to address this problem.

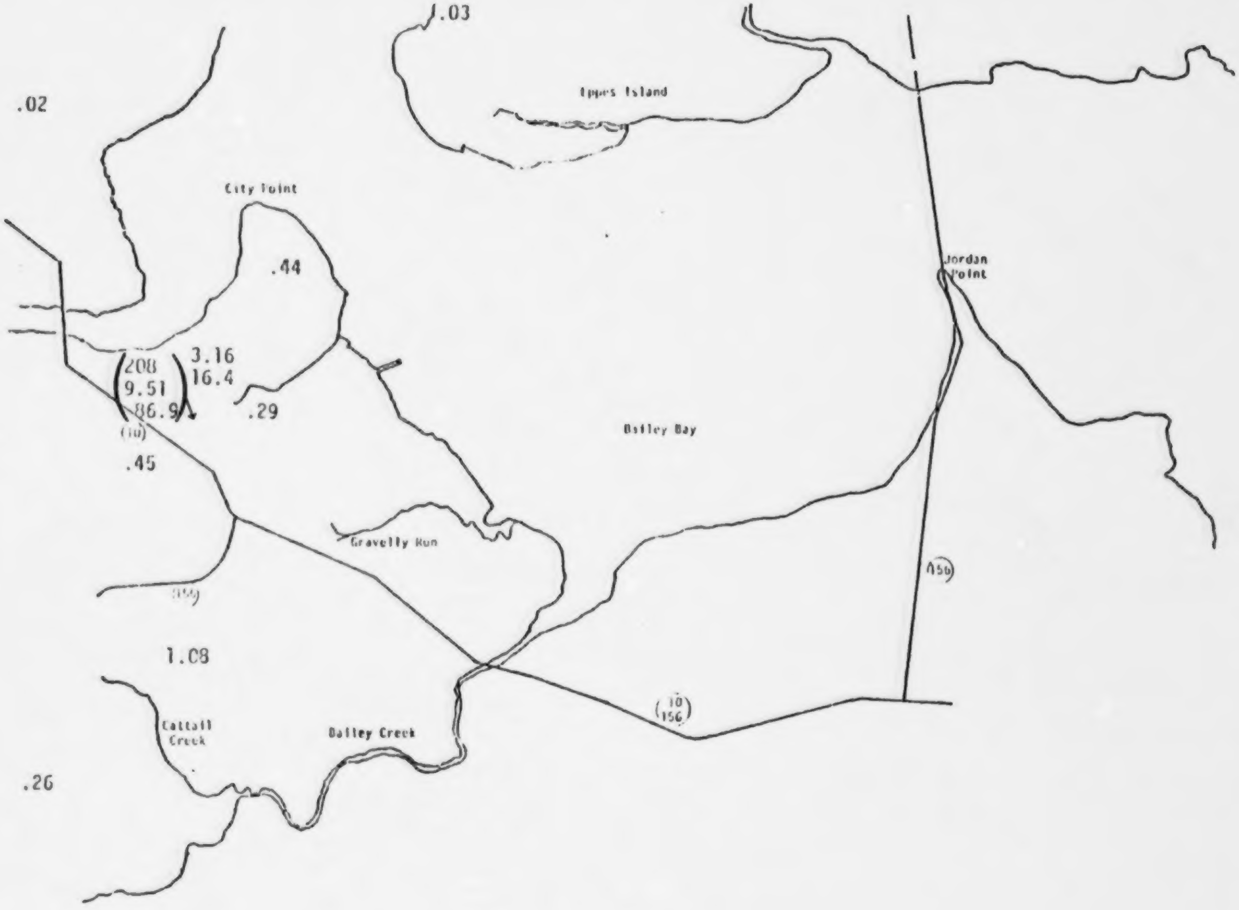

.02
.03
Eppes Island
City Point
.44
Jordan Point
208
9.51
86.9
3.16
16.4
.29
(10)
Bailey Bay
.45
Gravelly Run
(156)
(156)
10
156
1.08
Cattail Creek
Bailey Creek
.26

FIGURE 7. Kepone Concentrations in Soil in the Hopewell Area (μg/g-ppm)

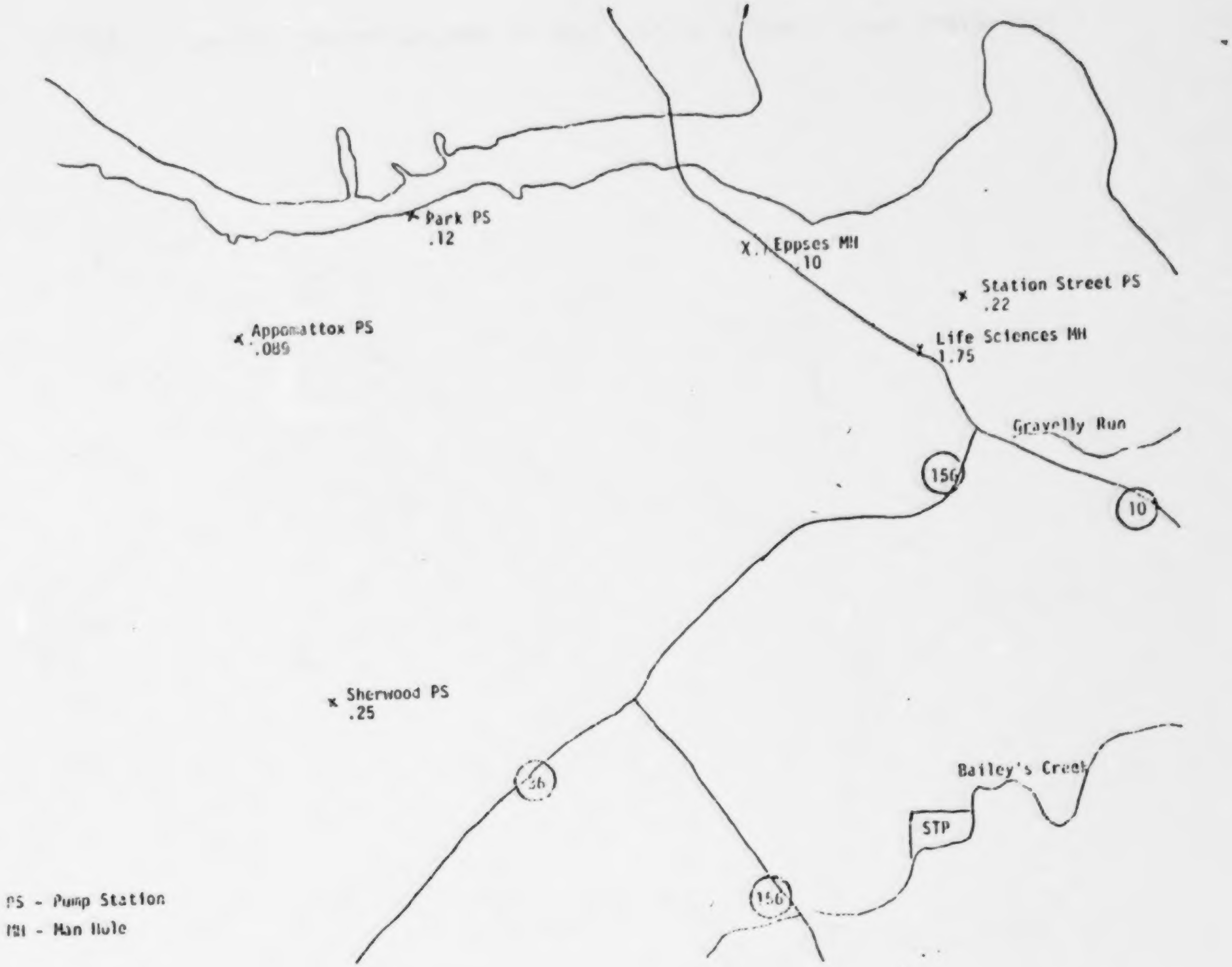

Park PS
.12
Eppses MH
.10
Station Street PS
.22
Appomattox PS
.089
Life Sciences MH
1.75
Gravelly Run
156
10
Sherwood PS
.25
36
Bailey's Creek
STP
156
PS - Pump Station
MH - Man Hole

FIGURE 8. Kepone Concentrations in Segments of Hopewell Sewer System (ppb)

MATHEMATICAL SIMULATION OF TRANSPORT OF KEPONE AND KEPONE-LADEN SEDIMENTS IN THE JAMES RIVER ESTUARY(a)

by

Yasuo Onishi

Richard M. Ecker

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(a) Publication of this paper requires final Battelle approval pending ERDA clearance

MATHEMATICAL SIMULATION OF TRANSPORT OF KEPONE AND KEPONE-LADEN SEDIMENTS IN THE JAMES RIVER ESTUARY

by

Yasuo Onishi
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Richland, Washington

SUMMARY

This paper describes the progress of a mathematical simulation study concerning kepone migration in the James River Estuary between Bailey Bay and the river mouth. The simulation is currently underway by applying the finite element sediment and contaminant transport model, FETRA, to solve time-dependent, longitudinal and lateral distributions of sediments and kepone by taking into account sediment-kepone interaction. The FETRA code solves sediment transport for three sediment types (i.e., cohesive and non-cohesive sediments, and organic materials). The model also solves kepone transport for dissolved and particulate (attached to sediments) kepone. Particulate kepone is analyzed for those adsorbed by sediment of each sediment type. The accuracy and convergence of the FETRA code were tested for simple one- and two-dimensional equations. These test results indicated excellent agreement between the computer solutions and exact analytical solutions.

INTRODUCTION

Kepone originally released into the James River estuarine system has been dispersed by turbulent mixing, river inflow and tidal flow. Much of the kepone has been adsorbed by river sediments (both organic and inorganic materials) which may create a significant pathway to man through the aquatic biota. Adsorption by the suspended sediments and/or possible desorption from them are important mechanisms affecting the migration of kepone through the James River estuarine system.(1,2) This is seen by the deposition and resuspension of contaminated sediments in the river.

In this study, the mathematical simulation of kepone migration in the James River Estuary is being conducted by applying the finite element sediment and contaminant transport model, FETRA,(3) to the river between Bailey Bay and the river mouth. Model computations are being initiated to solve time-dependent, longitudinal and lateral distributions of sediments and kepone by taking into account sediment-kepone interactions. Sediment transport is being modeled for three sediment types (i.e., cohesive and noncohesive sediments and organic matter), and simulation of kepone transport is being initiated for dissolved and particulate kepone (attached to sediments). Particulate kepone is being analyzed separately for that adsorbed by sediment in each sediment type.

MATHEMATICAL MODEL FORMULATION

Longitudinal and lateral distributions of sediments and kepone concentrations are being simulated by the FETRA model. The modeling procedure involves simulating the transport of sediments (organic and inorganic materials) within the water body. The results will then be input to models of dissolved and particulate kepone in order to observe the interaction between sediment and kepone. Finally, changes in river bed conditions will be recorded, including: 1) river bottom elevation change, 2) ratio of cohesive sediment, noncohesive sediment and organic material, and 3) distribution of kepone in the river bed.

This model is also applicable to other constituents, including nutrients, other pesticides, heavy metals, and radioactive materials, which may undergo physical-chemical reactions with the sediments.

Sediment Transport Model

Transport of cohesive sediment (silt and clay), noncohesive sediment (sand), and organic material (those being transported independently with sand, silt and clay) are modeled separately since movements of sediments and absorption capacity vary significantly. The model includes the effects of:

1. convection and dispersion of materials
2. fall velocity and cohesiveness
3. deposition on the river bed
4. resuspension from the river bed (bed erosion and armoring)
5. tributaries

Sediment mineralogy and water quality effects are implicitly included through the above mentioned effects 2, 3 and 4.

Governing Equations. The governing equation of sediment transport for the three dimensional case is:

$$\frac{\partial C_j}{\partial t} + \frac{\partial}{\partial x}(UC_j) + \frac{\partial}{\partial y}(VC_j) + \frac{\partial}{\partial z}\left\{(W - W_{s_j})C_j\right\}$$

$$= \frac{\partial}{\partial x}\left(\varepsilon_{x_j}\frac{\partial C_j}{\partial x}\right) + \frac{\partial}{\partial y}\left(\varepsilon_{y_j}\frac{\partial C_j}{\partial y}\right) + \frac{\partial}{\partial z}\left(\varepsilon_{z_j}\frac{\partial C_j}{\partial z}\right) \qquad (1)$$

where

C_j = concentration of sediment of jth type (weight of sediment per unit volume of water)

t = time

U = velocity component of longitudinal (x) direction

V = velocity component of lateral (y) direction

W = velocity component of vertical (z) direction

W_{s_j} = fall velocity of sediment particle of jth type

x,y,z = longitudinal, lateral and vertical direction in Cartesian coordinates, respectively

$\varepsilon_{x_j}, \varepsilon_{y_j}, \varepsilon_{z_j}$ = diffusion coefficients of longitudinal, lateral and vertical directions for jth sediment type.

Boundary conditions are:

$$(W - W_{s_j})C_j - \varepsilon_{z_j}\frac{\partial C_j}{\partial z} = 0 \qquad \text{at } z = h \qquad (2)$$

$$(1-\gamma)\, W_{s_j}C_j + \varepsilon_{z_j}\frac{\partial C_j}{\partial z} = S_{D_j} - S_{R_j} \qquad \text{at } z = 0 \qquad (3)$$

$$\frac{\partial C_j}{\partial y} = 0 \qquad \text{at } y = 0 \text{ and } B \qquad (4)$$

where

B = width of the river

S_{D_j} = sediment deposition rate per unit bed surface area for jth sediment type

S_{R_j} = sediment erosion rate per unit bed surface area for jth sediment type

γ = coefficient, i.e., probability that particle settling to the bed is deposited.

In this study, γ is assumed to be unity, that is, for the same flow condition all suspended matter settling to the river bed will stay on the river bed without returning to the flow. It is also assumed that the vertical flow velocity, W, is negligible.

Let

$$C_j = \bar{C}_j + c_j'' \tag{5}$$

$$U = \bar{U} + u'' \tag{6}$$

$$V = \bar{V} + v'' \tag{7}$$

$$\frac{\partial c_j''}{\partial x} = \frac{\partial c_j''}{\partial y} = \frac{\partial W_{s_j}}{\partial z} = 0 \tag{8}$$

where

$\bar{C}_j, \bar{U}, \bar{V}$ = depth averaged values of concentration of sediment for j^{th} type, longitudinal velocity, and lateral velocity, respectively

c_j'', u'', v'' = fluctuations from the depth averaged values of concentration of sediment of j^{th} type, longitudinal velocity, and lateral velocity, respectively.

By substituting the above expressions into Equation (1) and integrating it over the entire river depth, this equation becomes:

$$\begin{aligned}
&\bar{C}_j\left\{\frac{\partial h}{\partial t} + \frac{\partial}{\partial x}(\bar{U}h) + \frac{\partial}{\partial y}(\bar{V}h)\right\} - (\bar{C}_j + c_j'')\Big|_{z=h}\left\{\frac{\partial h}{\partial t} + (\bar{U} + u'')\Big|_{z=h}\frac{\partial h}{\partial x}\right.\\
&\left.\quad + (\bar{V} + v'')\Big|_{z=h}\frac{\partial h}{\partial y}\right\} + \left\{W_{s_j}(\bar{C}_j + c_j'')\Big|_{z=h} + \varepsilon_{z_j}\frac{\partial(\bar{C}_j + c_j'')}{\partial z}\Big|_{z=h}\right\}\\
&\quad = -h\left(\frac{\partial \bar{C}_j}{\partial t} + \bar{U}\frac{\partial \bar{C}_j}{\partial x} + \bar{V}\frac{\partial \bar{C}_j}{\partial y}\right) + h\frac{\partial}{\partial x}\left(\varepsilon_{x_j}\frac{\partial \bar{C}_j}{\partial x}\right) + h\frac{\partial}{\partial y}\left(\varepsilon_{y_j}\frac{\partial \bar{C}_j}{\partial y}\right)\\
&\quad - \frac{\partial}{\partial x}\int_0^h u''c_j''dz - \frac{\partial}{\partial y}\int_0^h v''c_j''dz - \left\{W_{s_j}(\bar{C}_j + c_j'')\Big|_{z=0}\right.\\
&\left.\quad + \varepsilon_{z_j}\frac{\partial(\bar{C}_j + c_j'')}{\partial z}\Big|_{z=0}\right\}
\end{aligned} \tag{9}$$

The equation of continuity, the kinetic water surface boundary condition and Equation (2) make the left side of Equation (9) zero. As in the Boussinesq diffusion coefficient concept, let

$$\int_0^h u''c_j''dz = (\overline{u''c_j''})h = - hD_{x_j} \frac{\partial \overline{C}_j}{\partial x} \tag{10}$$

and

$$\int_0^h v''c_j''dz = (\overline{v''c_j''})h = - hD_{y_j} \frac{\partial \overline{C}_j}{\partial y} \tag{11}$$

where D_{x_j} and D_{y_j} equal the dispersion coefficients of x and y directions for j^{th} sediment type. Hence Equations (2), (3), (9), (10), and (11) yield the following final expression of sediment transport:

$$\begin{aligned} &\frac{\partial \overline{C}_j}{\partial t} + \left(\overline{U} - \frac{D_{x_j}}{h}\frac{\partial h}{\partial x}\right)\frac{\partial \overline{C}_j}{\partial x} + \left(\overline{V} - \frac{D_{y_j}}{h}\frac{\partial h}{\partial y}\right)\frac{\partial \overline{C}_j}{\partial y} \\ &\quad = \frac{\partial}{\partial x}\left(K_{x_j}\frac{\partial \overline{C}}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_{y_j}\frac{\partial \overline{C}}{\partial y}\right) + \frac{S_{R_j}}{h} - \frac{S_{D_j}}{h} \end{aligned} \tag{12}$$

where

$$K_{x_j} = \varepsilon_{x_j} + D_{x_j}$$

$$K_{y_j} = \varepsilon_{y_j} + D_{y_j}$$

The finite element method was used to solve Equations (4) and (12).

Erosion and Deposition of Noncohesive Sediments (Sand). Erosion and deposition of noncohesive sediments are affected by the amount of sediment the flow is capable of carrying. For example, if the amount of sand being transported is less than the flow can carry for given hydrodynamic conditions, the river will scour sediment from the stream bed to increase the sediment transport rate. This occurs until the actual sediment transport rate becomes equal to the carrying capacity of the flow or until the bed sediments are all scoured, whichever occurs first. Conversely, the river deposits sand if its actual sediment transport rate is above the flow's capacity to carry sediment. DuBoys' formula(4) is used to estimate the flow capacity, Q_s, which is then compared with the actual amount of sand, Q_{sa}, being transported in a river water. Hence:

$$S_{R_j} = \frac{Q_s - Q_{sa}}{A} \tag{13}$$

$$S_{D_j} = \frac{Q_{sa} - Q_s}{A}$$

where

A = the river bed surface area.

Erosion and Deposition of Cohesive Sediments (Silt and Clay). Sediment erosion and deposition rates, S_{R_j} and S_{D_j}, are also evaluated separately for each sediment size fraction because erosion and deposition characteristics are significantly different for cohesive and noncohesive sediments. Since only Partheniades(5) and Krone(6) formulas for erosion and deposition rates, respectively, are presently available, these formulas were adopted in this study:

$$S_{R_j} = M_j \left(\frac{\tau_b}{\tau_{cR_j}} - 1 \right) \tag{15}$$

$$S_{D_j} = \frac{2W_{s_j}C_j}{h} \left(1 - \frac{\tau_b}{\tau_{cD_j}} \right) \tag{16}$$

where

M_j = erodibility coefficient for sediment of j^{th} type fraction

τ_b = bed shear stress

τ_{cD_j} = critical shear stress for sediment deposition for j^{th} sediment type fraction

τ_{cR_j} = critical shear stress for sediment erosion for j^{th} sediment type fraction.

Values of M_j, τ_{cD_j} and τ_{cR_j} must be determined by field and/or laboratory tests for a particular river regime. These values for the Columbia River (Washington) and the Clinch River (Tennessee) were reported in recent mathematical simulation studies concerning sediment and radionuclide transport in these two rivers.(7,8) The availability of bed sediments to be resuspended was also examined to determine the actual amount of sediment erosion.

When the fall velocity, W_{s_j}, depends on sediment concentration and no aggregation occurs, the fall velocity may be assumed:(6)

$$W_{s_j} = K_j C_j^{4/3} \tag{17}$$

where

K_j = an empirical constant depending on the sediment type.

Erosion and Deposition of Organic Materials. Recent studies(9,10) revealed that kepone is not only adsorbed by inorganic suspended sediment (mainly cohesive sediments) but also adsorbed by organic matter. Unfortunately, there have not been enough studies on transport characteristics of organic materials. Since the mechanics of erosion and deposition of organic matter are somewhat similar to those of cohesive fine sediment, Equations (15) and (16) are also utilized for this case. The selection of the values of W_{s_j}, M_j, τ_{cD_j} and τ_{cR_j} should reflect the characteristics of these materials, e.g., density, size, cohesiveness, compatibility, etc.

Dissolved Kepone Transport Model

In this study, it is assumed that the association of dissolved kepone with suspended sediments (both organic and inorganic matter) is the primary mechanism of kepone uptake, while direct uptake by biota accounts for a small percentage of the depletion. The model includes the effects of:

1. convection and dispersion of kepone within the river
2. adsorption (uptake) of dissolved kepone by sediments (cohesive and non-cohesive inorganic sediments and organic matter) or desorption from the sediments into water
3. chemical and biological decay of kepone
4. tributaries. (Kepone contributions from factories, overland runoff flow, fallout and groundwater to the James River system may be treated as a part of tributary contributions.)

Effects of water quality (e.g., pH, water temperature, salinity, etc.) and sediment characteristics, such as clay minerals, are taken into account through changes in the distribution (or partition) coefficient, K_{d_j}.

The governing equation of dissolved kepone transport for the three-dimensional case is:

$$\frac{\partial G_w}{\partial t} + \frac{\partial}{\partial x}(UG_w) + \frac{\partial}{\partial y}(VG_w) + \frac{\partial}{\partial z}(WG_w)$$

$$= \frac{\partial}{\partial x}\left(\varepsilon x_w \frac{\partial G_w}{x}\right) + \frac{\partial}{\partial y}\left(\varepsilon y_w \frac{\partial G_w}{\partial y}\right) + \frac{\partial}{\partial z}\left(\varepsilon z_w \frac{\partial G_w}{\partial z}\right)$$

$$- \lambda G_w - \sum_j (K_{d_j} C_j G_w - C_j G_j) \qquad (18)$$

In addition to the previously defined symbols:

K_{d_j} = distribution (or partition) coefficient between dissolved kepone and particulate kepone associated with j^{th} sediment.

G_j = particulate kepone concentration associated with j^{th} sediment (weight of kepone per unit weight of sediment)

G_w = dissolved kepone concentration (weight of kepone per unit volume of water)

$\varepsilon x_w, \varepsilon y_w, \varepsilon z_w$ = longitudinal, lateral and vertical diffusion coefficients for dissolved kepone

λ = chemical and biological decay rate of kepone.

Distribution coefficient, K_{d_j}, is defined by:

$$K_{d_j} = \frac{f_{s_j}/M_j}{f_w/V_w} = \frac{f_{s_j}}{f_w C_j} \qquad (19)$$

where

f_{s_j} = fraction of kepone sorbed by j^{th} sediment

f_w = fraction of kepone left in solution

M_j = weight of j^{th} sediment

V_w = volume of water

$$\frac{f_{s_j}}{f_w} = \frac{C_j G_j}{G_w}$$

Hence Equation (19) may be rewritten as:

$$G_j = K_{d_j} G_w \tag{20}$$

The adsorption of kepone by sediments or desorption from the sediments is assumed to occur toward an equilibrium condition if the particulate kepone concentration differs from its equilibrium values as expressed in Equation (20).

The boundary conditions for dissolved kepone transport are

$$WG_w - \varepsilon_{z_w} \frac{\partial G_w}{\partial z} = 0 \qquad \text{at } z = h \tag{21}$$

$$\frac{\partial G_w}{\partial z} = 0 \qquad \text{at } z = 0 \tag{22}$$

$$\frac{\partial G_w}{\partial y} = 0 \qquad \text{at } z = 0 \text{ and } B \tag{23}$$

Let:

$$G_w = \overline{G}_w + G''_w \tag{24}$$

$$\frac{\partial G''_w}{\partial x} = \frac{\partial G''_w}{\partial y} = 0 \tag{25}$$

where

$\overline{G}_w$ = depth averaged value of kepone concentration

G''_w = fluctuation from the depth averaged value of kepone concentration

By substituting the above expressions, together with those in Equations (5) through (8), into Equation (18) and integrating it over the entire river depth, Equation (18) becomes:

$$\bar{G}_w \left\{\frac{\partial h}{\partial t} + \frac{\partial}{\partial x}(\bar{U}h) + \frac{\partial}{\partial y}(\bar{V}h)\right\} - (\bar{G}_w + G_w'')\Big|_{z=h}\left\{\frac{\partial h}{\partial t} + (\bar{U} + u'')\Big|_{z=h}\frac{\partial h}{\partial x}\right.$$

$$\left. + (\bar{V} + v'')\Big|_{z=h}\frac{\partial h}{\partial y}\right\} + \left\{(\bar{W} + w'')(\bar{G}_w + G_w'')\Big|_{z=h} - \varepsilon_{z_w}\frac{\partial}{\partial z}(\bar{G}_w + G_w'')\Big|_{z=h}\right\}$$

$$+ \varepsilon_{z_w}\frac{\partial}{\partial z}(\bar{G}_w + G_w'')\Big|_{z=0}$$

$$= -h\left(\frac{\partial \bar{G}_w}{\partial t} + \bar{U}\frac{\partial \bar{G}_w}{\partial x} + \bar{V}\frac{\partial \bar{G}_w}{\partial y}\right) + D_{x_w}\frac{\partial h}{\partial x}\frac{\partial \bar{G}_w}{\partial x} + D_{y_w}\frac{\partial h}{\partial y}\frac{\partial \bar{G}_w}{\partial y}$$

$$+ h\frac{\partial}{\partial x}\left\{(\varepsilon_{x_w} + D_{x_w})\frac{\partial \bar{G}_w}{\partial x}\right\} + h\frac{\partial}{\partial y}\left\{(\varepsilon_{y_w} + D_{y_w})\frac{\partial \bar{G}_w}{\partial y}\right\}$$

$$- \lambda h\bar{G}_w - h\sum_j \bar{C}_j\,(K_{d_j}\bar{G}_w - G_j) \qquad (26)$$

where D_{x_w} and D_{y_w} are dispersion coefficients of x and y directions defined by:

$$\int_0^h u''G_w''\,dz = -h\,D_{x_w}\frac{\partial G_w}{\partial x} \qquad (27)$$

$$\int_0^h V''G_w''dz = -h\,D_{y_w}\frac{\partial \bar{G}_w}{\partial y} \qquad (28)$$

The equation of continuity, the kinetic water surface boundary condition and boundary conditions shown in Equations (21) and (22) then make the left side of Equation (26) zero. Hence, the final transport equation of dissolved kepone is:

$$\frac{\partial \bar{G}_w}{\partial t} + \left(\bar{U} - \frac{D_{x_w}}{h}\frac{\partial h}{\partial x}\right)\frac{\partial \bar{G}_w}{\partial x} + \left(\bar{V} - \frac{D_{y_w}}{h}\frac{\partial h}{\partial y}\right)\frac{\partial \bar{G}_w}{\partial y}$$

$$= \frac{\partial}{\partial x}\left(k_{x_w}\frac{\partial \bar{G}_w}{\partial x}\right) + \frac{\partial}{\partial y}\left(k_{y_w}\frac{\partial \bar{G}_w}{\partial y}\right) - \left(\lambda + \sum_j \bar{C}_j K_{d_j}\right)\bar{G}_w + \Sigma_j\,\bar{C}_j\,G_j \qquad (29)$$

where

$$k_{xw} = E_{x_w} + D_{x_w}$$

$$k_{yw} = E_{y_w} + D_{y_w}$$

The boundary conditions for this equation are those in Equation (23).

Particulate Kepone Transport Model

The transport model of kepone (or other constituents) attached to sediments are solved separately for those adsorbed by cohesive and noncohesive sediments, and organic materials (those being transported independently with the inorganic sediments). This model also includes the effects of:

1. convection and dispersion of particulate kepone
2. adsorption (uptake) of dissolved kepone by sediments or desorption from sediments into water
3. chemical and biological decay of kepone
4. deposition of particulate kepone on the river bed or resuspension from the river bed
5. tributaries. (Kepone contributions from factories, overland runoff flow, fallout and groundwater to the James River system may be treated as a part of the tributary contributions.)

As in the transport of sediments and dissolved kepone, the three-dimensional transport equation for kepone adsorbed by the jth sediment type (cohesive sediment, noncohesive sediment or organic materials) may be expressed as:

$$\frac{\partial C_jG_j}{\partial t} + \frac{\partial}{\partial x}(UC_jG_j) + \frac{\partial}{\partial y}(VC_jG_j) + \frac{\partial}{\partial z}\left\{(W - W_{s_j})C_jG_j\right\} = \frac{\partial}{\partial x}\left(\epsilon_{x_j}\frac{\partial C_jG_j}{\partial x}\right)$$

$$+ \frac{\partial}{\partial y}\left(\epsilon_{y_j}\frac{\partial C_jG_j}{\partial y}\right) + \frac{\partial}{\partial z}\left(\epsilon_{z_j}\frac{\partial C_jG_j}{\partial z}\right) - \lambda C_jG_j - (C_jG_j - K_{d_j}\, C_jG_w) \qquad (30)$$

where the kepone concentration, G_j, is assumed to be independent of z.(7,8) All symbols in Equation (30) were previously defined. Noting Equations (2), (3) and (4), boundary conditions for this case become:

$$(W - W_{s_j})\, C_j G_j - \varepsilon_{z_j} \frac{\partial C_j G_j}{\partial z} = G_j \left\{ (W - W_{s_j}) C_j - \varepsilon_{z_j} \frac{\partial C_j}{\partial z} \right\} = 0 \text{ at } z = h \qquad (31)$$

$$(1-\gamma)\quad W_{s_j} C_j G_j + \varepsilon_{z_j} \frac{\partial C_j G_j}{\partial z} = G_j S_{D_j} - G_{B_j} S_{R_j} \text{ at } z = 0 \qquad (32)$$

$$\frac{\partial C_j G_j}{\partial y} = C_j \frac{\partial G_j}{\partial y} + G_j \frac{\partial C_j}{\partial y} = C \frac{\partial G_j}{\partial y} = 0 \quad \text{Hence } \frac{\partial G_j}{\partial y} = 0 \text{ at } y = 0 \text{ and } B \qquad (33)$$

Equation (34) is derived by i) substituting Equations (5) through (8) into Equation (30), ii) integrating it over the river depth, iii) then substracting Equation (9) multiplied by G_j from the resulting equation, and iv) substituting the boundary conditions, Equations (31) and (32)

$$\frac{\partial G_j}{\partial t} + \left\{ \bar{U} - \frac{2\varepsilon_{x_j}}{\bar{C}_j} \frac{\partial \bar{C}_j}{\partial x} - \frac{D_{x_j}}{\bar{C}_j} \frac{\partial \bar{C}_j}{\partial x} + \frac{\varepsilon_{x_j}}{\bar{C}_j h} \frac{\partial h}{\partial x} \left(c''_j \big|_{z=h} \right) \right\} \frac{\partial G_j}{\partial x}$$

$$+ \left\{ \bar{V} - \frac{2\varepsilon_{y_j}}{\bar{C}_j} \frac{\partial \bar{C}_j}{\partial y} - \frac{D_{y_j}}{\bar{C}_j} \frac{\partial \bar{C}_j}{\partial y} + \frac{\varepsilon_{y_j}}{\bar{C}_j h} \frac{\partial h}{\partial y} \left(c''_j \big|_{z=h} \right) \right\} \frac{\partial G_j}{\partial y}$$

$$= \frac{\partial}{\partial x} \left(\varepsilon_{x_j} \frac{\partial G_j}{\partial x} \right) + \frac{\partial}{\partial y} \left(\varepsilon_{y_j} \frac{\partial G_j}{\partial y} \right) - \left(\frac{S_{R_j}}{\bar{C}_j h} + \lambda + 1 \right) G_j + \left(K_{d_j} G_w + \frac{G_{B_j} S_{R_j}}{\bar{C}_j h} \right) \qquad (34)$$

Since the two terms containing c" in the above equation are at least one order of magnitude smaller than the rest of the terms, these two terms may be deleted. Hence, the final expression becomes:

$$\frac{\partial G_j}{\partial t} + \left\{\bar{U} - \frac{2\varepsilon_{x_j}}{\bar{C}_j}\frac{\partial \bar{C}_j}{\partial x} - \frac{D_{x_j}}{\bar{C}_j}\frac{\partial \bar{C}_j}{\partial x}\right\}\frac{\partial G_j}{\partial x} + \left\{\bar{V} - \frac{2\varepsilon_{y_j}}{\bar{C}_j}\frac{\partial \bar{C}_j}{\partial y} - \frac{D_{y_j}}{\bar{C}_j}\frac{\partial \bar{C}_j}{\partial y}\right\}\frac{\partial G_j}{\partial y}$$

$$= \frac{\partial}{\partial x}\left(\varepsilon_{x_j}\frac{\partial G_j}{\partial x}\right) + \frac{\partial}{\partial y}\left(\varepsilon_{y_j}\frac{\partial G_j}{\partial y}\right) - \left(\frac{S_{R_j}}{\bar{C}_j h} + \lambda + 1\right) G_j + \left(K_{d_j} G_w + \frac{G_{B_j} S_{R_j}}{\bar{C}_j h}\right) \quad (35)$$

The boundary conditions for this case are those expressed in Equation (33).

Finite Element Method

High-speed digital computers have enabled engineers to employ various numerical discretization techniques for approximating solutions to complex mathematical equations. The finite element method is one such technique(11) and has recently gained popularity for solving both linear and nonlinear partial differential equations. Because of its increased solution accuracy and ready accommodation to various boundary geometrics,(7,8,12,13,14) this method is used for this study. The finite element solution technique with the Galerkin weighted residual method is used to solve Equations (12), (29) and (35) with the boundary conditions of Equations (4), (23) and (33).

The flow domain is divided into a series of triangular elements interconnected at node points. Six nodes are associated with each triangle, three at the vertices called corner nodes and three on the mid-sides called mid-side nodes. A quadratic approximation is made for the sediment and kepone concentrations within each element. Linear interpolation is used for the variation of flow depth and velocity within an element. A computer program is written in FORTRAN IV lagnguage to implement the model for a CDC 6600 computer. A more detailed description of the FETRA code programming is discussed in Onishi et al.(3)

EVALUATION OF THE FETRA MODEL

The accuracy and convergence of the numerical solutions calculated by the finite element sediment and contaminant transport model, FETRA, have been evaluated to confirm the validity of the basic computational scheme of the model. This verification involved solving equations by the FETRA code and comparing the resulting numerical solutions with known analytical solutions to the problems.

Unfortunately, the general unsteady two-dimensional convection-diffusion equation with decay and source (or sink) terms [e.g., Equations (29) and (35)] does not have known analytical solutions. Therefore, some simplified special cases were used for the analysis. The following three cases were selected as test cases.

Case 1

In this case the following one-dimensional steady convection-diffusion equation with a source term was solved:

$$U\frac{dC}{dx} = \varepsilon_x \frac{d^2C}{dx^2} + \beta \qquad (36)$$

with the boundary conditions of:

$$\left.\begin{aligned} C &= C_o \quad \text{at} \quad x = 0 \\ \frac{dC}{dx} &= 0 \quad \text{at} \quad x = \ell \end{aligned}\right\} \qquad (37)$$

An analytical solution to this problem is:

$$C = C_o + \frac{\beta\varepsilon_x}{U^2}\left[\exp\left(-\frac{U\ell}{\varepsilon_x}\right) - \exp\left[-\frac{U}{\varepsilon_x}(\ell - x)\right]\right] + \frac{\beta x}{U} \qquad (38)$$

Figure 1 shows computer results and the analytical solution, assuming;

$$U = 5.0,\ \varepsilon_x = 0.2,\ \beta = 2.0,\ C_o = 1 \text{ and } \ell = 1.0$$

An excellent agreement between these two solutions was obtained in this case.

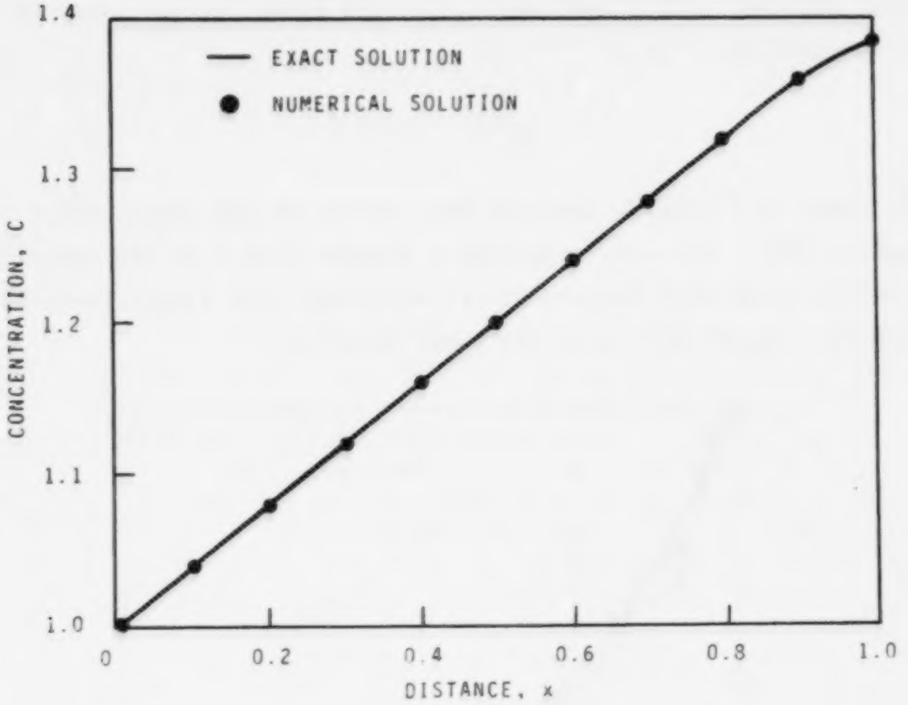

FIGURE 1. Comparison of Numerical Solution with Analytical Solution to One-Dimensional Steady Convection-Diffusion Equation with a Source Term

Case 2

In this case, convergence of a time-dependent, one-dimensional solution to a steady-state solution was tested. The governing equation was:

$$\frac{\partial C}{\partial t} = \varepsilon_x \frac{\partial^2 C}{\partial x^2} - \alpha C \tag{39}$$

with the following boundary conditions:

$$\left.\begin{array}{llll} C = 0 & \text{in} & 0 \leq x \leq \ell & \text{at} \quad t = 0 \\ C = C_o & \text{at} & x = 0 & \text{at} \quad t > 0 \\ \frac{\partial C}{\partial t} = 0 & \text{at} & x = \ell & \text{for all } t \end{array}\right\} \qquad (40)$$

Assuming $\varepsilon_x = 0.2$, $\alpha = 1.0$, $C_o = 1.0$ and $\ell = 1.0$, solutions are plotted in Figure 2, together with steady analytical and numerical solutions of the following equation;

$$\varepsilon_x \frac{\partial^2 C}{\partial x^2} - \alpha C = 0 \qquad (41)$$

As shown in Figure 2, there is convergence to the steady exact solution of Equation (41). For runs with time t greater than 4.0, the numerical solutions coincide with the analytical solution. The steady-state numerical solution also agrees well with the exact solution.

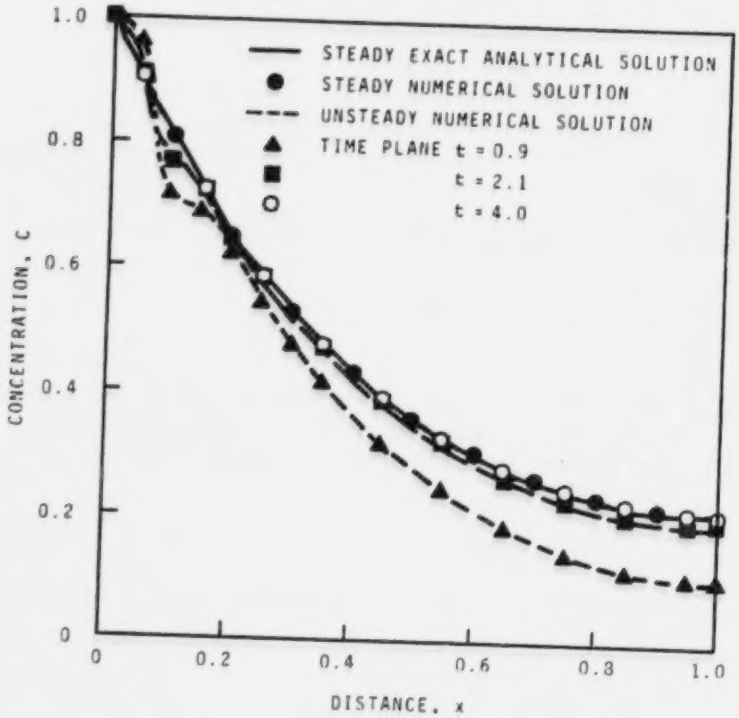

FIGURE 2. Convergence of Unsteady-State One-Dimensional Diffusion Equation to Steady-State Solution

Case 3

The following two-dimensional equation was solved numerically and computed results were compared with an analytical solution:

$$\varepsilon_x \frac{\partial^2 C}{\partial x^2} + \varepsilon_y \frac{\partial^2 C}{\partial y^2} = 0 \tag{42}$$

with boundary conditions of:

$$\left.\begin{array}{lll} C = 0 & \text{at} & x = 0 \\ C = 0 & \text{at} & x = \ell \\ C = 0 & \text{at} & y = 0 \\ C = C_o \sin(\frac{\pi x}{\ell}) & \text{at} & y = \ell \end{array}\right\} \tag{43}$$

where $\varepsilon_x = \varepsilon_y = \ell = 1.0$ and $C_o = 10$. The analytical solution for this case is:

$$C(x,y) = 0.866 \sinh(\pi y) \sin(\pi x) \tag{44}$$

The computer results and analytical solutions are shown in Figure 3. Numbers in the figure are values of concentration C. Since the solutions are symmetric with respect to $x = 0.5$, computer results are given in the region of $0.5 \leq x \leq 1.0$, and analytical solutions are plotted in the region of $0 \leq x < 0.5$. Comparison of these results reveals that there is an excellent agreement between the computed and analytical solutions.

As illustrated in Figures 1, 2, and 3, the agreements of the model solutions and the exact solutions were excellent. These results confirm the validity of the basic numerical computation scheme of the transport model, FETRA.

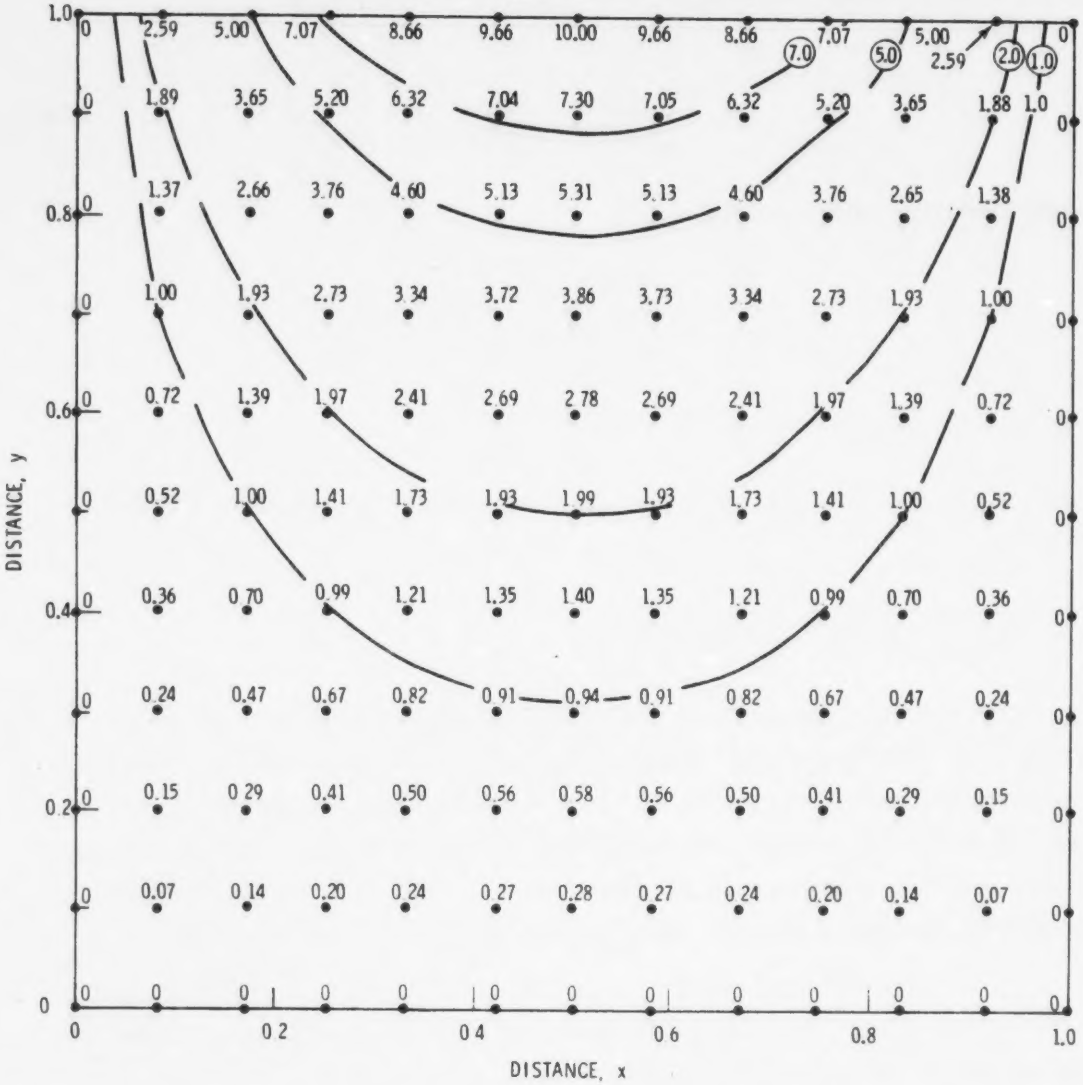

FIGURE 3. Comparison of Numerical Solution with Analytical Solution to Two-Dimensional Diffusion Equation

SIMULATION OF KEPONE TRANSPORT
IN THE JAMES RIVER ESTUARY

This section describes the present stage of the kepone simulation study using the FETRA code. Unfortunately, final simulation results are not available because preparation of input data is not complete at this time.

Input Data Requirements

Application of the FETRA code to simulate the movement and distribution of kepone in the 113 km (70 mile) stretch of the James River Estuary requires the input of certain physical, hydrodynamical and chemical data as initial conditions and for calibration of the model. These data include: information on depth variations of the waterway; tidal stage variations, flow characteristics; size distribution of suspended and bed sediments; suspended sediment load; critical shear stresses for cohesive sediment erosion and deposition and erodibility coefficient; initial distribution of kepone in the bottom sediments; initial kepone concentrations in the dissolved and particulate phase; and kepone distribution coefficients between sediment and water. Of particular concern is the behavior of organic matter which is believed to contain high levels of kepone.

The input data required for the FETRA code must, in most cases, be obtained in the field. Most past field data on sediment and kepone transport characteristics collected in the James River have not been for the specific purpose of input to the FETRA code and, therefore, lack some required parameters or are not of sufficient quantity to meet the input data requirements. The following is the specific requirements of the FETRA code.

a. Channel Geometry - Depth and width data are required as an initial input condition. From the initial depth conditions the model accounts for temporal variations in bottom elevation as a result of deposition and erosion of bed sediments.

b. Hydrodynamics - Water surface elevations and the longitudinal-lateral flow field are input data for the FETRA code. These data must reflect the tidal flow regime of the area to be modeled. The required hydrodynamic data are presently being developed by application of Leenderstse's unsteady two-dimensional, long-period wave (tidal) propagation model.(15) Diffusion and dispersion coefficients are also required.

c. Suspended Sediment Load - Suspended sediment data are required as an initial condition to the FETRA code and for adjustment of the critical shear stresses for erosion and deposition of cohesive and organic sediments. Since one of the primary functions of the FETRA code is the simulation of total suspended and bed-load sediments (both organic and inorganic materials) transport, it is important that the time-dependent longitudinal and lateral variations in the suspended sediment load be reflected in the FETRA code. Figures 4a, 5a and 6a are examples of the longitudinal and lateral distribution of suspended sediment load at maximum flood, maximum ebb and slack water conditions measured on 25 through 28 June 1977. Size characteristics of suspended sediments and organic matter for the initial condition are also important input parameters to allow for variations in settling velocities and settling characteristics of different types of sediments and organic materials.

d. Bottom Sediment Characteristics - Longitudinal, lateral and vertical size characteristics of bottom sediments are an important initial input condition for the FETRA code so as to allow for a realistic simulation of erosion of the sediment bed under varying flow conditions. Bed sediment types must be categorized into cohesive and non-cohesive sediments, and organic material in order for the FETRA code to realistically simulate erosion and deposition of bed sediments.

e. Chemical Characteristics - Since the primary objective of the modeling effort is to simulate the movement and distribution of kepone, initial input data to the FETRA code must include the distribution of kepone in bed sediments, suspended sediments and dissolved kepone. Figures 4b, 5b,

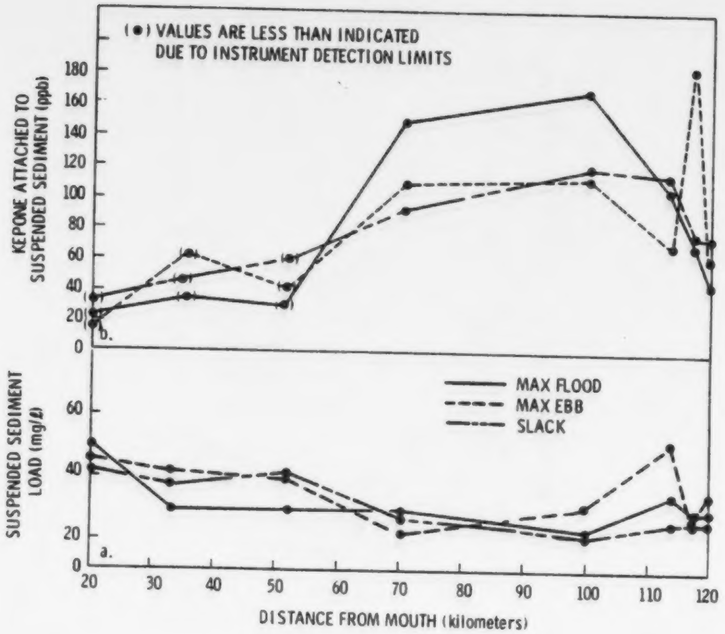

FIGURE 4. Longitudinal Variations in Suspended Sediment and Kepone Attached to Suspended Sediment

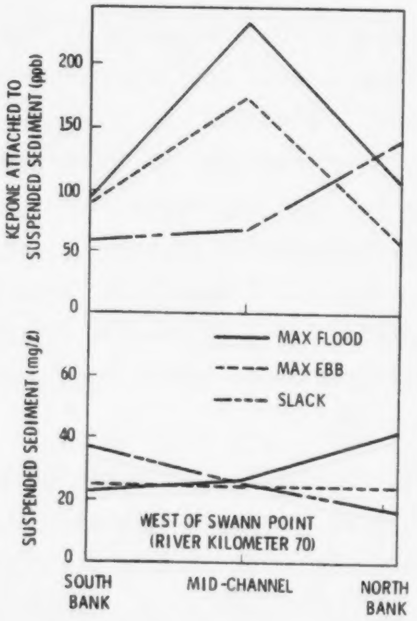

FIGURE 5. Lateral Variations in Suspended Sediment and Kepone Attached to Suspended Sediment

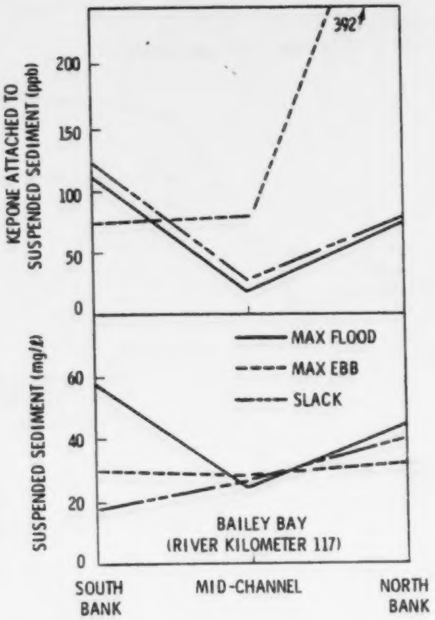

FIGURE 6. Lateral Variations in Suspended Sediment and Kepone Attached to Suspended Sediment

and 6b are examples of the type of data required by the FETRA code as an initial condition for the longitudinal and lateral distribution of kepone attached to suspended sediment. Figure 7 is an example of kepone in the bed sediments of Bailey Bay. Furthermore, the particulate kepone (attached to suspended and bed sediments) must be broken down into that portion attached to each sediment type, i.e., noncohesive sediment (sand), cohesive sediments (silt, clay) and organic fractions. Figure 8 is an example of the depth distribution of kepone at Jordon Point (River Kilometer 114) and Figure 9 is an example of the depth distribution of kepone by size fraction west of Swann Point (River Kilometer 70).

Much of the above data, especially that pertaining to chemical characteristics, is lacking or is just now becoming available. The accuracy of the simulation results depends in large part on the availability of these input data.

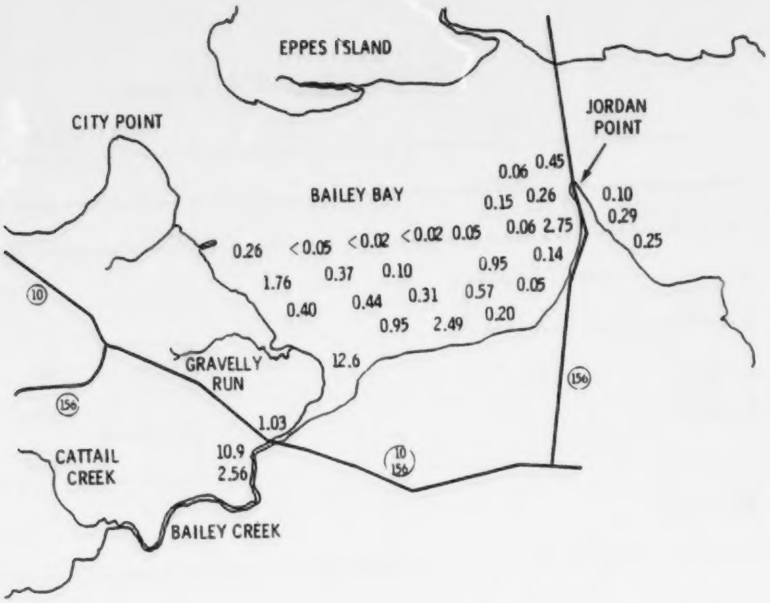
EPPES ISLAND
CITY POINT
JORDAN POINT
BAILEY BAY
0.06
0.45
0.15
0.26
0.10
0.29
0.25
0.26
<0.05
<0.02
<0.02
0.05
0.06
2.75
1.76
0.37
0.10
0.95
0.14
0.40
0.44
0.31
0.57
0.05
0.95
2.49
0.20
10
156
GRAVELLY RUN
12.6
1.03
CATTAIL CREEK
10.9
2.56
10
156
BAILEY CREEK

FIGURE 7. Areal Distribution of Kepone in First Ten Inches of Bottom Sediments

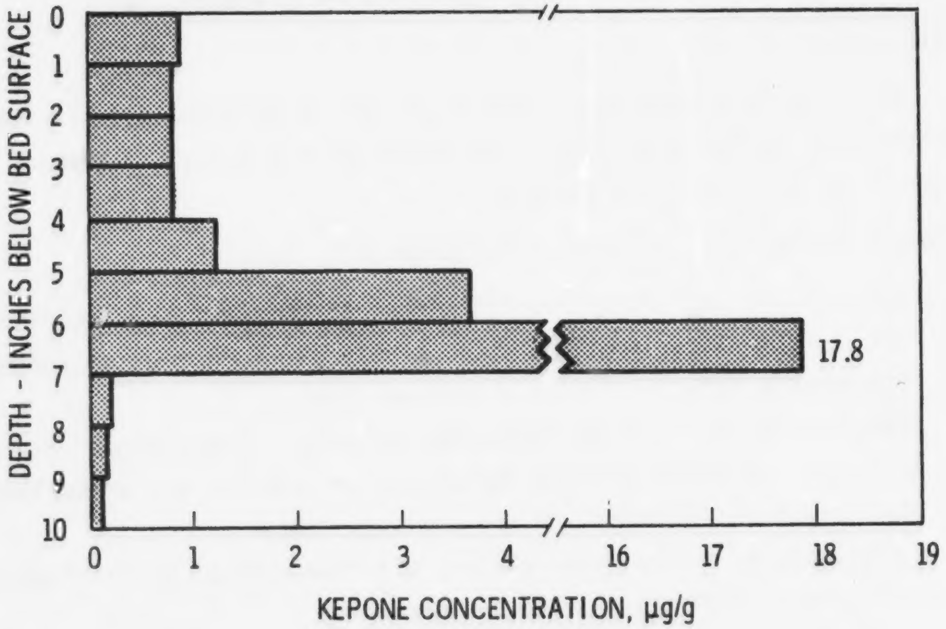

FIGURE 8. Depth Distribution of Kepone (All Fractions) - Jordon Point (River Kilometer 114)

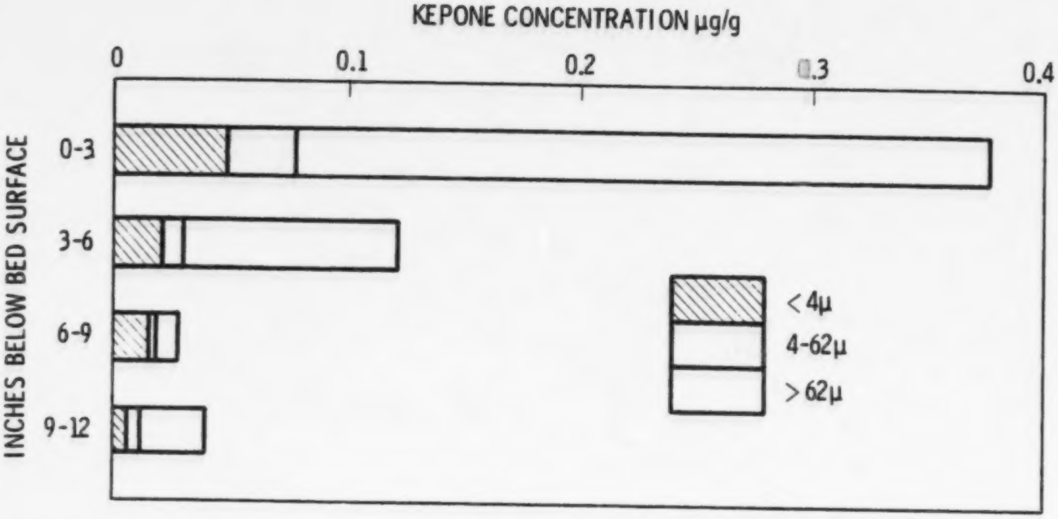

FIGURE 9. Depth Distribution of Kepone by Size Fraction - West of Swann Point (River Kilometer 70)

Model Output

With the data input described above, the FETRA code will simulate the sediment and kepone movements in the James River Estuary. A summary of the computer simulation output follows.

Sediment Simulation. Sediment simulation will include:

1. longitudinal and lateral distributions of sediment load (suspended and bed load) for each sediment type (cohesive and noncohesive sediments, and organic materials) at any assigned time,
2. longitudinal and lateral variations of noncohesive sediment and organic matter at an assigned river bed elevation (changes due to sediment deposition and/or scour) at any assigned time,
3. longitudinal, lateral and vertical distributions of weight fraction ratio among sediments at any assigned time.

Kepone Simulation. Kepone simulation will include:

1. longitudinal and lateral distributions of dissolved kepone concentration at a given time,
2. longitudinal and lateral distributions of concentration of kepone adsorbed by each sediment type at a given time,
3. longitudinal, lateral and vertical distributions of kepone concentrations in the river bed associated with each sediment type at a given time.

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PRELIMINARY EVALUTATION OF APPROACHES TO THE AMELIORATION OF KEPONE CONTAMINATION[a]

by

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[a] Publication of this paper requires final Battelle approval pending ERDA clearance.

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INTRODUCTION

Historically, dredging has been employed as a means of moving large quantities of sediments which, by their presence, impact the use and efficiency of channels and harbors. More recently, dredging has also been looked to as a means of physically removing sediments contaminated with persistent toxicants which resist natural degradation processes. The continued presence of the latter threatens water quality and the viability of associated aquatic communities. Dredging, however, is not always well suited to the task. Standard dredging operations have always been plagued by problems of induced turbidity from resuspended particulate matter. The increased solids-water contact may also stimulate resolubilization of attached contaminants. In either case, the potential exists for intensifying short-term hazards as well as for translocating toxic materials to other potentially uncontaminated areas. These possibilities suggest caution in whole-sale application of dredging technology to situations of contamination from in-place toxics.

It is also important to note that dredging alone is not a complete solution. One must supplement it with an acceptable means of disposing of the spoils. Traditional practices for creating spoil disposal sites may simply not be adequate since they do not accomodate the treatment of leachate which will often carry toxicants back to nearby waterways.

These considerations are of particular concern with respect to kepone contamination in the James River. Should dredging be selected as the preferred method for removing kepone from the James, there will be great concern on both accounts: 1) Will dredging activities facilitiate movement of kepone residuals from current locations downstream to presently uncontaminated regions in the River and Chesapeake Bay? and 2) Is it realistic to assume that the massive quantity of spoils which would result from dredging can be disposed of and that subsequent leaching will not redistribute the kepone back to the river system?

As an integral part of the process to answer these questions, it is necessary to evaluate the existence of alternatives to dredging as well as the consequences of taking no assertive action in the river, thus allowing natural dissipative and degradative mechanisms to cleanse the river over time. The work reported herein was focused on evaluating alternatives to dredging as well as treatment and/or fixation processes complementary to dredging for application to kepone contaminated sediments in the James River System. The work has involved laboratory and evaluation studies by a number of different groups. Three types of alternatives were studied: 1) those which could be used to fix dredge spoils for disposal, 2) those which could be employed to treat elutriate or spoils slurries, and 3) those which could be applied in situ as substitutes to dredging. Individual options identified within each of these categories are discussed below.

DREDGE SPOIL FIXATION

It has long been known that the disposal of toxic liquids on sludges into land disposal sites can lead to groundwater and airborne contamination due to leaching by natural precipitation and resuspension by wind. Consequently, various materials have been identified as stabilization or fixation agents capable of solidifying these wastes and in so doing, minimizing subsequent movement of contaminants. Candidate materials include asphalt, tar polyolefins, epoxy resins, silicates, and elemental sulfur. The desireability of any one fixation agent is based on the characteristics of the contaminant to be bound as well as the conditions of disposal which may lead to a breakdown of the structure of the fixed mass.

In the past, fixation processes hare largely been applied to wastes containing inorganic contaminants such as heavy metals.(1) In this context, the silicates have been relatively successful. For instance, cadmium from electroplating sludge leached at much slower rates when fixed than it did from raw sludge.(2) Success has also been reported using a polybutadiene binder resin and a polyethylene encapsulating agent on toxicants such as copper, chromium, zinc, nickel, cadmium, mercury and monosodium methanearsenate.(3) Little, however, has been done to measure the effectiveness of these agents to retard the leaching of persistent organic contaminants. Therefore, it was necessary to conduct a series of laboratory studies to evaluate the effectiveness of fixation agents on reducing leachate kepone concentrations from contaminated sediments.

Procedures

Each fixation agent being evaluated has been subjected to two types of standardized tests: 1) a short term elutriate test, and 2) a longer term leach test. The results of these will then be employed to assess the overall effectiveness of a particular set of fixation agents. High levels resulting from the elutriate assessment reflects potential to cause immediate impact. Contamination of leachate carries longer term implications. All fixation work was performed on a "standard" sediment prepared through homogenization of a large sample of Bailey Bay sediments. The kepone concentration in these samples has been measured at 1 ppm (μg/g).

The standard elutriate test employed for these studies was modeled after a procedure described by Keeley and Engler(4) from work at the U.S. Army Engineer Wasteways Experiment Station. Specific changes include an increase in the water to sediment volumetric ration from 1:4 to 1:19 as recommended by Lee, et al.(5) This reduction to a five percent slurry is made to accomodate lower total contaminate levels in the elutriate as a result of reduced solubilities characteristic of chlorinated hydrocarbons. The elutriate pH was also modified. Based on work by Esmen and Fergus,(6) distilled water with an adjusted pH of 4.5 was employed to simulate rainfall. This simulates the most common conditions expected in industrialized areas.

Based on these modifications, elutriate tests were conducted as follows:

1. All samples were held at 4°C prior to testing.
2. Fixed sediments were then ground to pass a 10 mesh screen.

3. Distilled water at pH 4.5 was then added to the ground sediment at 19 parts water to 1 part sediment (5 percent).
4. The slurry was then mixed vigorously for 30 minutes on a horizontal displacement mechanical mixer.
5. Mixtures were then allowed to settle for one hour.
6. Settled slurries were centrifuged at 3,500 rpm for 30 minutes and centrate filtered through a .7-2μ Gelman glass fiber filter.
7. Finally, filtrate was analyzed for kepone and compared to results obtained with unfixed sediments.

Similar considerations were made in designing the leach test employed. Specific steps included:

1. All samples were held at 4°C prior to testing.
2. Blocks of fixed sediments were weighed and reduced in size to the diameter of pea gravel or less.
3. Approximately 70 gm of particles were then placed in sealed leaching bottles and 500 ml of distilled water at pH 4.5 was added.
4. At each sampling interval, the water is removed from the vessel, and a new pH 4.5 500 ml aliquot is added.
5. Removed aliquots are split. Half are sent for kepone analysis, and half are composited to assess total kepone losses.
6. Sample intervals were selected as 1, 4, and 24 hours; 7, 14, 28, and 84 days.

Results to Date

Only commercially available fixation agents were employed for the studies reported here. To identify candidates and avoid arbitrary exclusion of any options, an attempt was made to contact all companies currently marketing fixation processes. Firms identified for this purpose and their subsequent response are detailed in Table 1. All companies were offered the opportunity to participate, but as is evident from Table 1, not all chose to do so.

Preliminary data are available on silicate and gypsum based sealants from three firms. These are presented in Table 2. None of the samples exhibit any clear retardation of kepone loss. Indeed, several agents appear to enhance leachability. For the silicate agents this is believed to reflect

TABLE 1. Candidate for Fixation Agent Testing on Kepone Contaminated Sediments

Company	Address	Response
Chemfix-National Environmental Controls, Inc.	Metairie, LA	Fixed samples at company
TJK Ind.	7407 Fulton Ave. North Hollywood, CA 91605	Fixed samples at company and sent chemicals for in-house fixation
IU Conversion System	Plymouth Meeting, PA	No response
Protective Packaging	Louisville, KY	Not developed enough for testing on sediments
John Sexton Landfill Contractors	Oakbrook, IL	No response
Werner and Pfluidores, Corp.	Waldwick, NJ	No response
Wehran Engineering Corporation	Middletown, NY	No response
Ontario Liquid Waste Disposal Systems	470 Collier MacMillan Dr. P.O. Box 1060 Cambridge, Ontario	Fixed samples at company
TRW Inc.	Redondo Beach, CA	Not developed enough for testing on sediments
Manchek Colorado	P.O. Box 30737 Santa Barbara, CA	Fixed samples at company
Key Chemicals	4346 Tacony St. Philladelphia, PA	Sending samples of sediment fixed at company
Dowell Division, Dow Chemical	Tulsa, OK	Sent chemicals
Hallemite Division, Sterling Drug Co.	225 Summit Ave Montvale, NJ 07645	Sent chemicals
Randustrial Corp	13311 Union Ave Cleveland, OH	Sent chemicals
Tidewater Terminal Co.	Pasco, WA	Sent asphalt sample
Surcoat	Chevron San Francisco, CA	No response

TABLE 2. Kepone Concentrations in Leachate Solutions (ppb)

Fixation Type[a]	Leach Period in Hours					
	1	4	24	168	336	672
Company A - Silicate 1	1.04	0.99	1.01	1.81	1.74	2.09
Silicate 2	1.34	2.64	0.90	1.30	1.18	0.78
Silicate 3	1.33	1.88	1.31	1.42	1.04	1.02
Silicate 4	0.39	0.54	1.00	1.18	1.27	1.41
Company B - Silicate 1	0.07	0.08	0.094	0.166	0.524	0.30
Silicate 2	0.05	0.05	0.111	0.157	0.306	0.27
Company C - Gypsum	0.52	0.47	0.91	0.91		
Blank 1	<0.06	<0.06	0.076	0.058	0.050	0.22
Blank 2	0.117	0.04	0.104	0.081	0.11	

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[a] Company names will not be identified until data are finalized and firms have been informed of their products performance.

the high pH associated with the fixation process. The low pH leachate appears to break the fixed particle down. Further, since kepone is much more soluble under high pH conditions, the fixation process is actually releasing kepone from sediments. The gypsum system also appears to physically breakdown when left standing in water. A preliminary evaluation of asphalt binders was made, but these could not be easily mixed with wet sediments unless heated. This is believed to constitute excessive costs and equipment requirements for the volumes of sediments involved.

ELUTRIATE/SLURRY TREATMENT

Should dredging be employed to restore the James River system, there will be a need for the capability to treat elutriate, leachate, and/or the entire dredge spoil slurry in order to prevent subsequent escape and movement of low level contamination. The applicability of various approaches depend completely on the physical-chemical properties of the kepone as well as the nature of the liquid stream to be treated. For the purposes of the work conducted here, candidate approaches were divided between biochemical and physical-chemical mechanisms.

Biochemical Approaches

A review of the literature was conducted to determine if biological interactions have any potential for application to kepone amelioration. In general, there is a paucity of data upon which any detailed analysis can be conducted. However, sufficient information on the properties of kepone and the related compounds mirex and kelevan do exist for a preliminary assessment.

No evidence of microbial dehalogenation of kepone could be found in the literature. Work by Vind(7) in both aerobic and anaerobic seawater solutions over a 12 month period produce no measureable kepone reduction. Similarly, Brown et al.(8) and Jones and Hodges(9) were unsuccessful in obtaining degradation of Mirex with various strains of aerobic and anaerobic organisms from soils and sediments. However, Andrade et al.(10-11) do report anaerobic conversion of Mirex to the 10-monohydride derative in a sewage sludge. Kelevan, which contains an ethyl levulimate functional group, is much more susceptible to degradation.(12) The residuals, however, are measured as kepone.

Water with fungi and molds would appear to be more productive. Dr. Ralph Vallentine of Atlantic Research reports that upon screening some 40 strains of fungi and mold, he was able to identify 6 which yielded 13-40 percent degradation over a 2-3 week period. Results were best when no additional carbon source was available to the organism. The intermediate degradation products were identified. The approach bears promise for work with waste materials.

Physical-Chemical Systems

Numerous means exist for the physical-chemical destruction of organic materials. A wide range of these were evaluated for application to kepone contaminated water and sediments. Subsets of these include approaches designed around the use of oxidizing chemicals and processes utilizing electromognetic waves of various frequencies.

The simplest option classified in the latter category is photodegradation with straight sunlight. No data were found with respect to the effect of light on kepone degradation. Some work has been performed on mirex. In these studies it was determined that mirex is not subject to photolysis to any great extent.(13-15) However, significant enhancement of the photolysis process was achieved when the mirex was placed in an aliphatic amine solution.(13) The decomposition product appeared to be a mixture of monohydride derivatives.

To test the applicability of this process to kepone, 10 ppm in solutions of 100 and 10 percent amine were exposed to a sunlamp for 1 hour. Results are summarized in Table 3. The ethylenedisamine shows promise at higher concentrations. Work is currently underway to identify degradation products, assess the effectiveness of other secondary amines, and evaluate the concept for application to contaminated soils.

Use of γ radiation can also effect degradation, but required doses are considered too high for consideration. A residual of .14 ppm was obtained when sediment with 1.2 ppm kepone was subjected to 144 megarad. This is equivalent to 88 percent removal.

TABLE 3. Effects of Sunlamp Irradiation in Amine Solutions

Solvent System	Strength of Solvent (%)	Kepone Concentration in ppb After 1 Hour	Kepone Concentration in ppb After 23 Hours
Hexane	10	1,640	6,040
	100	3,700	530
Ethanolamine	10	2,230	7,970
	100	6,520	2,530
Triethylamine	10	54.4	18,620
	100	2,240	477
Ethylenediamine	10	1,715	117
	100	<22.9	

Work has also been performed on ozone enhanced ultraviolet oxidation. This is a process presently under development at Westgate Research in West Los Angeles, California. In a preliminary evaluation with a stock solution of 5.172 ppm, residuals of 20.9 ppb and 46.7 ppb were obtained over 1.5 and 2 hour exposures, respectively. A second set of tests is currently underway with waters having a high particulate load. This is of concern because of the need for the UV to penetrate the slurry being treated.

Chemical oxidation tests were conducted with chlorine dioxide (ClO_2) and ozone. Neither oxidant was effective in degrading kepone. A second set of evaluations with ClO_2 in sunlight is now underway. Work is underway at Envirogenics to determine the effectiveness of their catalytic reduction process for dechlorination. No data are available at this time.

IN SITU PROCESSES

In situ processes as a category are the newest of the approaches to removal/mitigation of in-place toxic materials. As such, they are typically not as fully developed as other approaches, but may offer benefits as yet unmeasured. Several of the more promising options were selected for testing in the laboratory.

A preliminary assessment suggested that biological approaches hold little promise for use in areas where kepone contamination is of concern. While Atlantic Research has identified six strains of fungi and mold capable of degrading kepone, all appear to be subject to dominence by natural bacteria in sediments. Therefore, application in situ would be hampered by poor growth if not total loss of viability.

It has also been suggested that biological systems could be used to accumulate the kepone and then be harvested for retrieval. For instance, algae has been shown to accumulate kepone by a factor of up to 800.(17) The concentration of kepone in the water of Bailey Bay, however, was found to be 10^{-4} the concentration in the sediments. The algae can concentrate kepone from the water, but not the sediment. Consequently, extensive amounts of time would be required to accumulate all of the deposited kepone from Bailey Bay.

Recent reports have also documented the use of macroaquatic plants to remove organic contaminants such as PCB's from water.(19) The same time constraints plague this option as discussed previously for algae. Advantage could be gained if rooted plants were capable of accumulating kepone from sediments in a similar fashion. When tested in the laboratory, however, it was found that barley did not translocate kepone to the stem and leafy parts. Uptake occurs only in the roots where the mechanism is likely to be direct adsorption rather than biological uptake.

Artificial means of accumulation may be more promising. Natural sorbents such as activated carbon and synthetic sorbents such as the macroreticular resins have been shown to be effective in concentrating organics similar kepone. Indeed, in preliminary laboratory investigations, several commercial agents were found to have a partition coefficient 100 times that for Bailey Bay sediments. It was further determined, that through incorporation of magnetite into the structure of the sorbent beads, these particles could be spread through an area of contaminated sediments and selectively retrieved after a period of accumulation. To test this concept, a series of aquariums were prepared containing "standard" sediment holding 1.2-1.5 ppm kepone. To each of these, a commercial sorbent was added at 1 part per 100 parts sediment and allowed to stand. At preset intervals, aquariums were drained and the sorbent removed to allow analysis of the sediment and a regenerate solution from the resin. Preliminary results for the first time periods are presented in Table 4. The 863 and XAD-2 sorbents appear quite effective. They also display continued effectiveness beyond the initial two week period. There is some concern, however, that such a process will be kinetically limited. The sorbent can quickly remove dissolved kepone from interstitial waters, but this is only a minute portion of the total quantity in the system. Subsequent removal requires desorption and migration to the sorbent. To study the nature of such movement, vertical columns of contaminated sediment were designed and a sorbent layer placed on the surface. After 8 weeks, 0.5 inch segments were sectioned and analyzed independently to determine the depth of influence. Results are presented in Table 5. The 863 appears to have been effective at least to a depth of 3.5 inches. Additional analysis at increasing depths is presently underway so as to determine the ultimate depth of influence.

It is also possible to physically retard the availability of kepone to the water column. This approach has been tested on mercury contaminated sediments using polymer films(17) and on PCB contaminated sediments in Japan using an in situ stabilization technique.(18) An assessment of the former approach revealed some promise for use of a 2 mil sheet of polyethylene in the Bailey Bay area. Venting to relieve pressure from anaerobic generation of gases, however, may reduce effectiveness. The in situ stabilization technique is still under study to determine the effectiveness of the silicate based agents.

None of the elutriate treatment processes evaluated have shown potential for use in situ.

PRELIMINARY ASSESSMENT

Results and status of candidate alternatives evaluated to date are summarized in Table 6. No fixation agents have been found satisfactory to date, but several have yet to be fully evaluated. Apparent problems with the more common silicate based agents stem from kepone desorption at the higher pH

TABLE 4. Effectiveness of Sorbents in Accumulating Kepone from Bailey Bay Sediments

	2 wk Exposure		4 wk Exposure	
	Conc. in Sediment After 2 wk, µg/ℓ	Apparent Removal, %	Conc. in Sediment, µg/ℓ	Apparent Removal, %
XADZ(a)	0.80	49	0.53	66
XAD4(a)	1.18	24	1.06	32
863(b)	0.89	43	0.72	54
FILTRASORB(c) 300	1.21	22	1.06	32
Magnetic Carbon	1.56	0	1.23	21
Blank	1.56	0	1.56	

(a) Product of Rohm and Haas
(b) Product of Diamond Shamrock
(c) Product of Calgon

TABLE 5. Effect of Surface Application of Sorbents with Depth

		Sorbent 863(a)		XAD-4(b)	
Depth, in.	Blank Kepone Content, ppm	Kepone Content, ppm	Apparent % Removal	Kepone Content, ppm	Apparent % Removal
0.5		0.079	70	0.291	--
1.0	0.262	0.060	77	0.209	20
1.5		0.066	75	0.119	55
2	0.211	0.328	--	0.155	41
2.5		0.045	79	0.053	75
3.0		0.299	--	0.174	34
3.5		0.040	81	0.233	--
4.0				0.058	73

(a) Product of Diamond Shamrock

(b) Product of Rohm and Haas

TABLE 6. Summary of Results and Status of Candidate Alternative Evaluations

Approach	Option	Results	Status
Fixation	Silicate Bases	High pH characteristics produce expensive leachate concentrations	Some agents still to be tested
	Gypsum Bases	Breakdown in water, ineffective	Rejected
	Epoxy Bases		Tests not complete
	Sulfur Bases		Tests not complete
	Asphalt	Too difficult to apply to wet sediments	Rejected
Electriate Slurry Treatment	Amine Photolysis	Some degradation rated with specific amines	Testing degradation products and applicability
	γ Radiation	Effective at excessive doses	Rejected
	UV-Ozonolysis	Effective on clear solutions	Testing in natural waters
	Ozone	Ineffective	Rejected
	Chlorine Dioxide	Ineffective	Testing in presence of sunlight
	Catalytic Reduction		Data not yet available
	Biological Degradation	Promising strains of fungi and mold identified	Deserves further consideration
In situ	Biological	No significant degradation, bioaccumulation bad, harvesting too slow from sediments	Rejected
	Retrievable synthetic sorbents	Specific media highly effective	Tests are continuing
	Polymer films	Feasible	Assessing probable effectiveness, long-term implications

levels. At least three candidate elutriate/slurry treatment processes have shown promise to date: UV ozonalysis, biodegradation with selected fungi and molds, and amine assisted photolysis. Retrievable synthetic sorbent and polymer films both appear applicable as in situ approaches at this time.

The information presented here is preliminary in nature. Many analytical data are yet to be evaluated and numerous tests must still be completed. Only after these have been concluded and viewed collectively can recommendations be made for implementation of mitigation activities on the James River.

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SESSION III

"Related Sediment Contamination Problems"

CHAIRMAN

Dr. Leo J. Hetling
Director
Bureau of Water Research
New York State Department of Environmental Conservation

SPEAKERS

Edward G. Horn, Ph.D.
Research Scientist III
Bureau of Water Research
New York State Department of Environmental Conservation
"Hudson River - PCB Study Description and Detailed Work Plan"

T. J. Tofflemire, Dr. Engr.
Research Scientist III
Bureau of Water Research
New York State Department of Environmental Conservation
"Hudson River Sediment Distributions and Water Interactions Relative to PCB - Preliminary Indications"

Russell C. Mt.Pleasant
Director
Bureau of Monitoring and Surveillance
New York State Department of Environmental Conservation
and
Carl Simpson, Ph.D.
Research Scientist II
Environmental Health Center
New York State Department of Health
"The Use of Artifical Substances for Monitoring Toxic Organic Compounds: Preliminary Evaluation Involving the PCB Problem in the Hudson River"

Paul M. Griffen
Manager
Separation Technology Project
Research and Development Center
General Electric Company
"Research Progress on Removal or Treatment of PCB in Hudson River Sediment"

HUDSON RIVER - PCB
STUDY DESCRIPTION AND
DETAILED WORK PLAN

Edward G. Horn
and
Leo J. Hetling

INTRODUCTION

On September 8, 1976 the New York State Department of Environmental Conservation and the General Electric Company signed an agreement bringing to a close the action brought against General Electric relating to the discharge of polychlorinated biphenyls (PCBs) into the Hudson River. This paper presents a detailed description of the Department of Environmental Conservation's program for implementing Section 3 of the settlement which is the portion related to monitoring and reclamation of the river.

BACKGROUND

Polychlorinated biphenyls (PCBs) were first manufactured in 1929 and their chemical properties were soon discovered to be ideal for a number of industrial uses. They are extremely stable chemically and biologically, conduct electricity very poorly,and possess a very low solubility in water. In the United States,they have been used for a wide variety of purposes, most heavily as a heat transfer fluid and insulator in heavy electrical equipment. But, these same chemical properties create a significant biological hazard.

This hazard might have gone unnoticed had it not been for an industrial accident in Japan that has come to be called the Yusho ("rice oil disease") incident. In 1968 this disease (manifest primarily as a serious skin disorder) was traced to PCB contamination of rice oil during its manufacture. Since that incident, more research has turned up rather frightening facts.

Yusho victims are still exhibiting symptoms of the poisoning and, even though not exposed to additional PCBs, they still have high levels of PCBs in their blood and other body tissues. Several deaths among the victims have been associated with malignant cancers, though it is not possible to conclusively state that the PCBs caused the cancers. Recent evidence shows that the rice oil and tissues of Yusho patients also contained polychlorinated dibenzofurans (PCDFs). PCDFs are more toxic than PCBs. It is therefore not possible to conclusively associate the symptoms of this incident with PCB poisoning.(1,2)

Experiments with laboratory animals, including monkeys, however, confirm that many of the symptoms associated with Yusho are directly related to consumption of PCBs and persist in the bodies of all experimental animals long after they are removed from diets containing PCBs. In addition to deaths being noted at high doses, liver tumors have also been induced in mice and rats. An exhaustive summary of these effects can be found in the recent Criteria Document for PCBs (1976) published by the Environmental Protection Agency(1) and a report published by the United States Department of Health, Education and Welfare(2).

As a result of accumulating research on PCB toxicity, the United States Food and Drug Administration (FDA) has set standards for allowable levels of PCBs in various foods.(3)

THE PCB SETTLEMENT

Polychlorinated biphenyls were discovered to be a problem in the Hudson River in 1975. The United States Environmental Protection Agency and Fish and Wildlife Service analyzed samples of fish taken from the river and found that PCB concentrations were higher than the FDA limits by a substantial margin. The fish could thus not legally be shipped for interstate sale. Acting on this and additional evidence that the Department of Environmental Conservation (DEC) had itself collected, charges were brought against the General Electric Company (GE) for polluting the river with the toxic substance PCB. Administrative proceedings began on September 8, 1975. On February 9, 1976, after weeks of testimony and a substantial record of several thousand pages of transcripts, prefiled testimony, reports, studies and other exhibits, the Hearing Officer, Professor Abraham D. Sofaer, found that DEC had presented overwhelming evidence of GE's responsibility for high concentrations of PCBs in the upper Hudson's waters, sediment, organisms and fish. In a 77-page interim opinion, Professor Sofaer detailed the evidence and the violations(4). It is interesting to note that he found that the unlawful actions were the consequence of both corporate abuse and regulatory failure by the responsible Federal and State agencies.

In order to determine the appropriate remedial measures, a second phase of the hearing was held during the spring and summer of 1976. As a result of this hearing, a settlement agreeable to all parties was negotiated and finalized exactly one year after the administrative proceedings began, September 8, 1976(5).

The settlement calls for a comprehensive program of at least $7 million to deal with PCBs in the Hudson River and related environmental concerns. General Electric was required to reduce its PCB discharges, which had been averaging about 30 pounds per day until 1972, to one pound per day beginning September 8, 1976, and to construct a wastewater treatment facility at the Hudson Falls and Fort Edward Capacitor Manufacturing Facilities. Total PCB discharges from the plants were reduced to one gram (0.022 pounds) per day by May 1977.

The agreement stipulated that GE was to cease using PCBs by July, 1977 and to perform $1 million of research on several items including the environmental compatibility of any substitute. Finally, GE was required to contribute $3 million to the Department as its share of additional work to further monitor the presence and levels of PCBs; to investigate the need for remedial action concerning PCBs present in the Hudson and to implement such action, if necessary; and to aid in developing a program to regulate the storage and discharge of substances hazardous to the environment. New York State was, by the agreement, obligated to provide an additional $3 million for this work and the Commissioner of Environmental Conservation became responsible for overseeing and expediting the required work. An overview of the provisions of the settlement related to studies of the Hudson River and the Department's activity to date in implementing them is shown in Table 1.

ADVISORY COMMITTEE

A key provision of the settlement is an Advisory Committee consisting of independent experts and governmental and private interests which was established to "review and make public recommendations to the Commissioner concerning the scope, content, progress and results of the programs, studies and expenditures".

The PCB Settlement Advisory Committee has been appointed and meets monthly to carefully evaluate the work in progress and make recommendations regarding results and further studies.

The relationship of this Advisory Committee to the Department and implementation of the settlement is given in Figure 1.

THE HUDSON RIVER PROBLEM

In order to better understand the Hudson River PCB problem, it is useful to know something about the river itself.

For most purposes, the Hudson River Drainage Basin can be divided into three sub-basins - the Upper Hudson River, the Mohawk River and the Lower Hudson River as shown in Figure 2.

Table 2 shows the relative area and water flows for these three basins. From Ft. Edward to Cohoes the Upper Hudson River is actually a series of low

Table 1

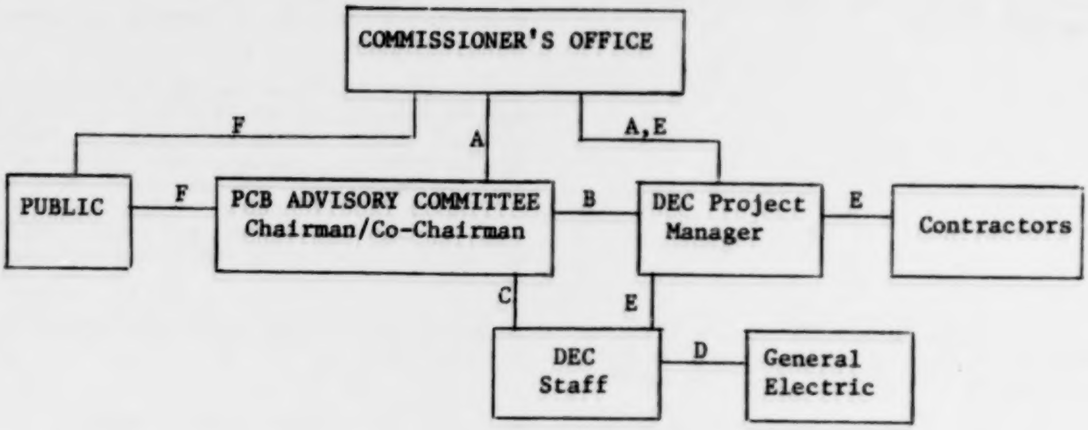
Overview of Task Required by Section 3 of PCB Settlement

Settlement Provisions	Department Activity to Date
I. Advisory Committee	
The Commissioner of Environmental Conservation will establish an Advisory Committee consisting of independent experts, governmental and private interests which will, at regular meetings review and make public recommendations to the Commissioner concerning the scope,content, progress and results of the program, studies and expenditures for which provision is made in the agreement.	An Advisory Committee has been formed and it meets regularly.
II. Other Funds	
In the event that the funds herein provided for implementing remedial actions concerning PCBs present in the Hudson River shall be inadequate to assure protection of public health and resources, then the Department will use its best efforts to obtain additional funds from sources other than GE, that are necessary to assure such protection.	No action can be taken until a decision as to the need for and cost of specific remedial action is made.
III. Overall River Program	
1. Monitor the presence and levels of PCBs which have been discharged in Hudson River waters in water, sediment and biota.	A monitoring program has been developed by the Dept. and approved by the Advisory Committee. This program includes contracts for PCB mapping with Normandeau Assoc., PCB lab analysis with O'Brien and Gere, and water and sediment transport measurements with USGS. An extensive program of fish, macroinvertebrate, water and air monitoring by the Dept. is also underway. EPA special core study of estuary section was carried out in December 1976. Lamont-Doherty Lab will carry out studies to follow-up the results of this survey. For more detail see Table 3.

Settlement Provisions	Department Activity to Date
2. Further investigate the need for remedial action concerning PCBs present in the Hudson River.	Contracts for studies relating to taking no remedial actions and to removal of PCB contaminated sediments by dredging are underway (see Figure 5). The Advisory Committee has approved maintenance dredging by DOT of a small section of the east channel of the river near Ft. Edward. An environmental assessment for this project has been prepared(6,7) and approved. Dredging is expected to take place during the summer of 1977. Experience from this project will be useful in evaluating and design of future projects.
3. Implement remedial action if necessary to protect public health and resources, concerning PCBs present in the Hudson River.	No action can be taken until above studies are received.
4. Aid in developing a program to regulate the storage and discharge of substances hazardous to the environment if sufficient monies are available after implementing remedial action concerning PCBs.	No action can be taken until a remedial action program is decided upon and implemented; however, an overall Hudson River research program is being prepared by the Advisory Committee.
IV. Work to be Carried out by GE ($1 million)	
GE will conduct research itself or by contract on the environmental compatibility of its substitute non-PCB dielectric capacitor fluids ($400,000).	A substantial amount of work on the substitute has been done by GE. A preliminary report(8) on the substitutes has been published and is under review.
GE will conduct research to be approved prior to being undertaken by the Commissioner after his consultation with the Advisory Committee on the removal or treatment of PCBs in supernatant liquids and sediments from the Hudson River sludge ($400,000).	The work study plan(9) presented by GE has been approved by the Commissioner on the recommendation of the Advisory Committee and work is underway.
GE will conduct research as specified by the Commissioner of the effects on the environment of not more than three substances which may be hazardous to the environment and which are to be selected by the Commissioner after his consultation with the Advisory Committee ($200,000).	The Advisory Committee has been asked to recommend three substances for study. They have established a subcommittee for this task.

Figure 1

Organizational Chart for the PCB Settlement Between General Electric and The Department of Environmental Conservation


COMMISSIONER'S OFFICE
F
A
A,E
PUBLIC
F
PCB ADVISORY COMMITTEE Chairman/Co-Chairman
B
DEC Project Manager
E
Contractors
C
E
DEC Staff
D
General Electric

A. Give advice and respond to questions.

B. Managerial direction
   1. Advise DEC about short-term and long-term planning.
   2. Receive and react to periodic reports from DEC staff.
   3. Assist DEC in evaluations.
   4. Assist DEC in preparing reports and recommendations to the Commissioner.

C. Technical resource.

D. Exchange of information.

E. Managerial direction.

F. Public access and information.

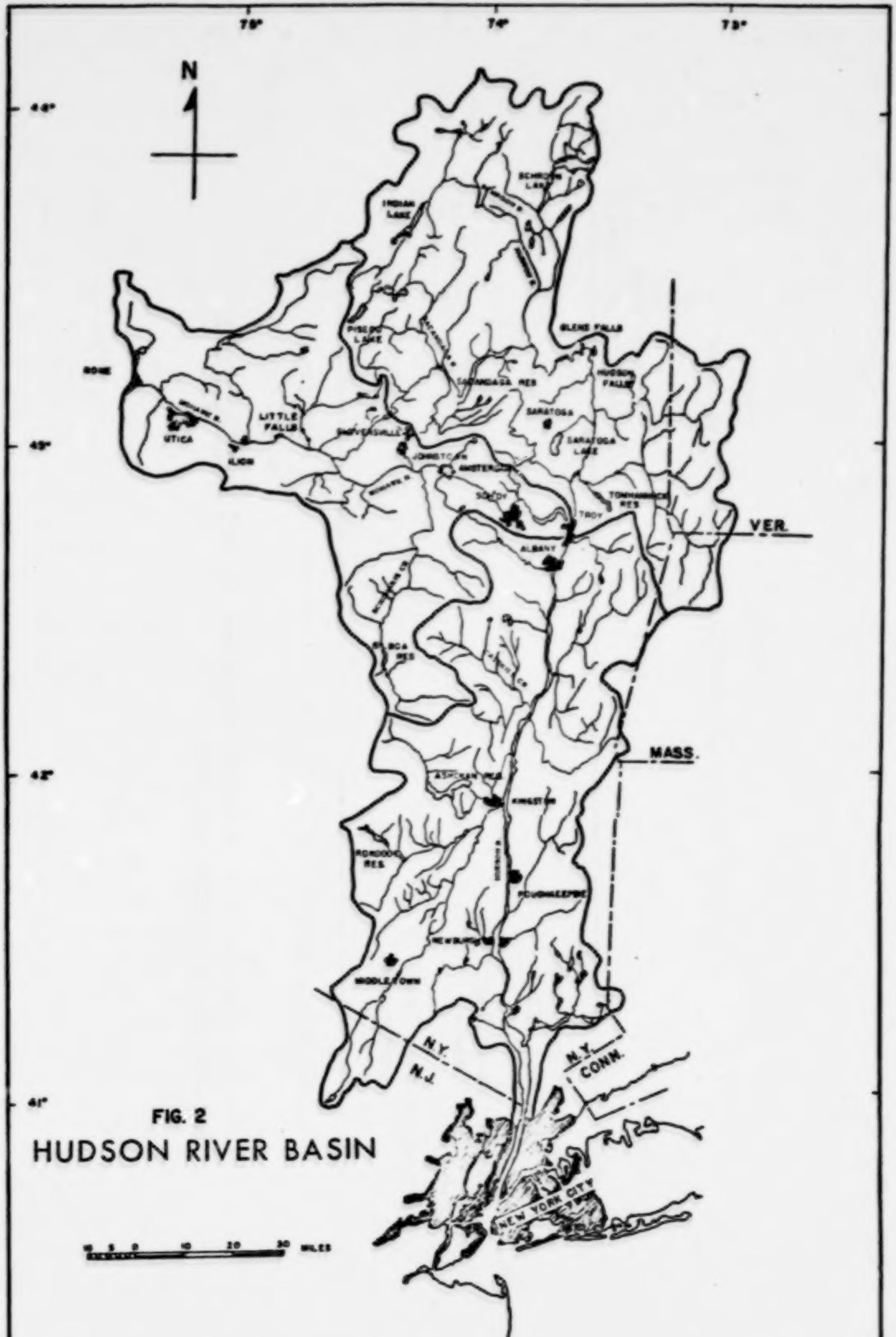

75°
74°
73°
44°
43°
42°
41°
N
ROME
UTICA
ILION
LITTLE FALLS
INDIAN LAKE
SCHROON LAKE
PISECO LAKE
GLENS FALLS
HUDSON FALLS
SACANDAGA RES
SARATOGA
SARATOGA LAKE
GLOVERSVILLE
JOHNSTOWN
AMSTERDAM
SCHDY
TROY
TOMHANNOCK RES
ALBANY
VER.
GILBOA RES
MASS.
ASHOKAN RES
KINGSTON
RONDOUT RES
POUGHKEEPSIE
NEWBURGH
MIDDLETOWN
N.Y.
N.J.
N.Y.
CONN.
NEW YORK CITY
10 5 0 10 20 30 MILES

FIG. 2

HUDSON RIVER BASIN

Table 2

Hudson River Drainage Basin Area and Average Flow

Location	Area		Average Flow	
	mi^2	km^2	ft^3/sec	m^3/sec
Upper Hudson Basin Waterford	4,634	12,002	7,660	217
Mohawk River Basin Cohoes	3,456	8,951	5,630	159
Lower Hudson Basin Tributaries	5,300	13,727	7,100	201
Total Hudson Basin	13,390	34,680	20,390	577

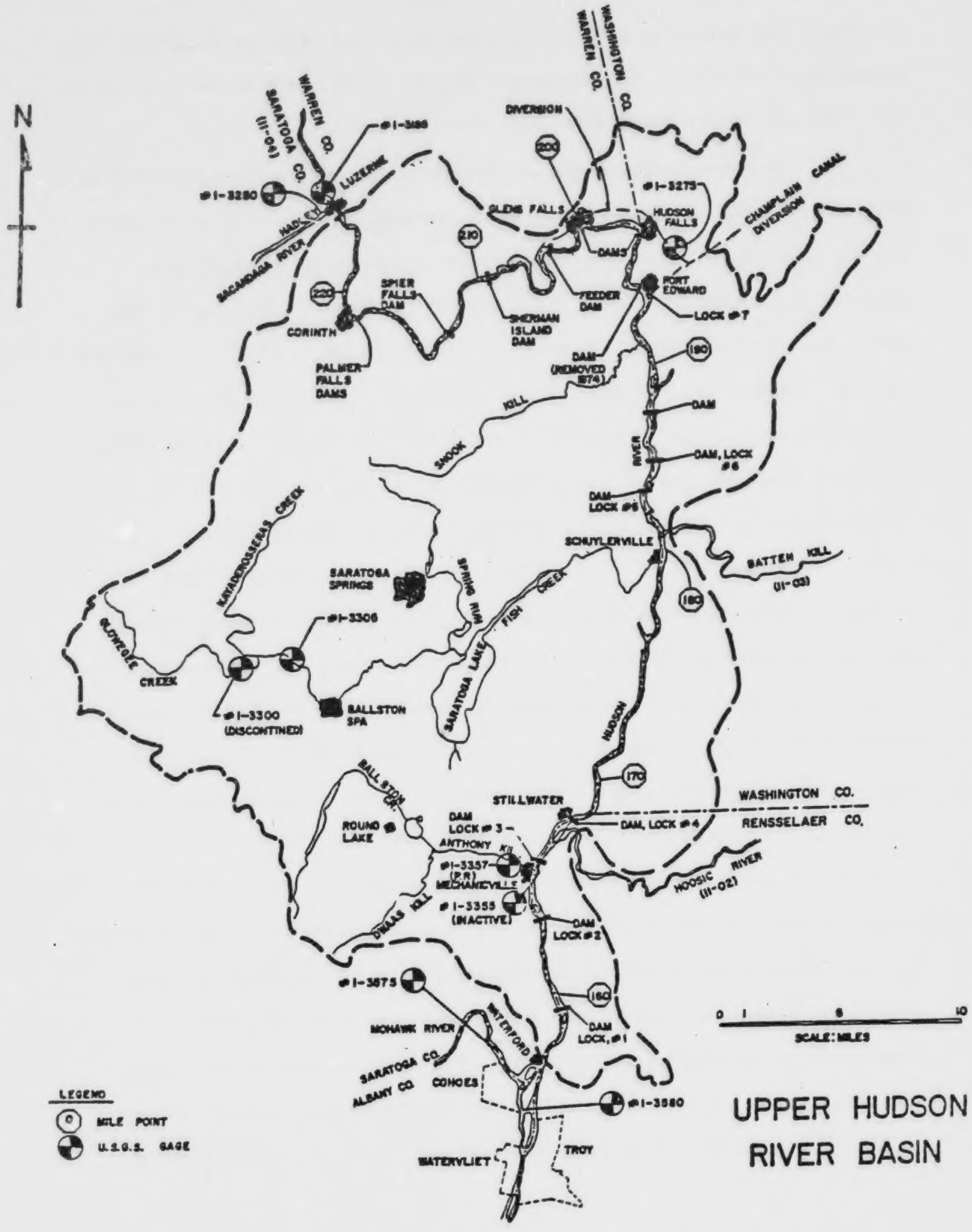
--from U.S. Department of Interior, Geological Survey, Water Resources Data for New York Water Year 1975, 1976.

level dams and serves as part of the Champlain Canal (Figures 3 and 4). The Mohawk River serves as the eastern portion of the New York State Barge Canal and joins the Hudson River just above the Troy Dam.

The lower Hudson Basin is tidal over its entire 150 miles (241 km). Average tides are 4.4 feet (1.4 m) at the Battery, 3.0 feet (1 m) at Beacon and 4.8 feet (1.5 m) at Troy. Tidal flows at Poughkeepsie have been measured as 230,000 to 280,000 cfs (6,516-7,932 cms). Dye studies have shown that the flow actually oscillates with the tide, with a very slow net outflow. Because of this tidal flow, salt-water intrusion extends quite a distance upriver. The 50 mg/l (0.05 o/oo) salinity fluctuates from 20 mi. (32.2 km) above the Battery (near Tappan Zee Bridge) to 70 mi. (112.7 km) inland (south of Poughkeepsie) depending on the freshwater flow.

Testimony given at the hearing clearly demonstrates that although the levels of PCBs in fish and other animals are alarming, most of the PCBs are held in the sediments on the river bottom and suspended in the water. Very little PCBs can be found in the water itself, but because of bioaccumulation, it is enough to create a serious hazard. "Clean" fish placed in this water in cages ("live-cars") have accumulated dangerous PCB levels in their flesh within one month(4).

Existing data indicates that the sediments in the section immediately below the GE discharges at Fort Edward are the most contaminated. General Electric discharged large volumes of PCBs for at least 25 years. Much of this probably accumulated in the sediments impounded behind the dams south of the manufacturing plants. The first dam was located in Fort Edward, but, for various reasons, it was removed in the late summer of 1973(10). Some of the contaminated sediment which subsequently moved

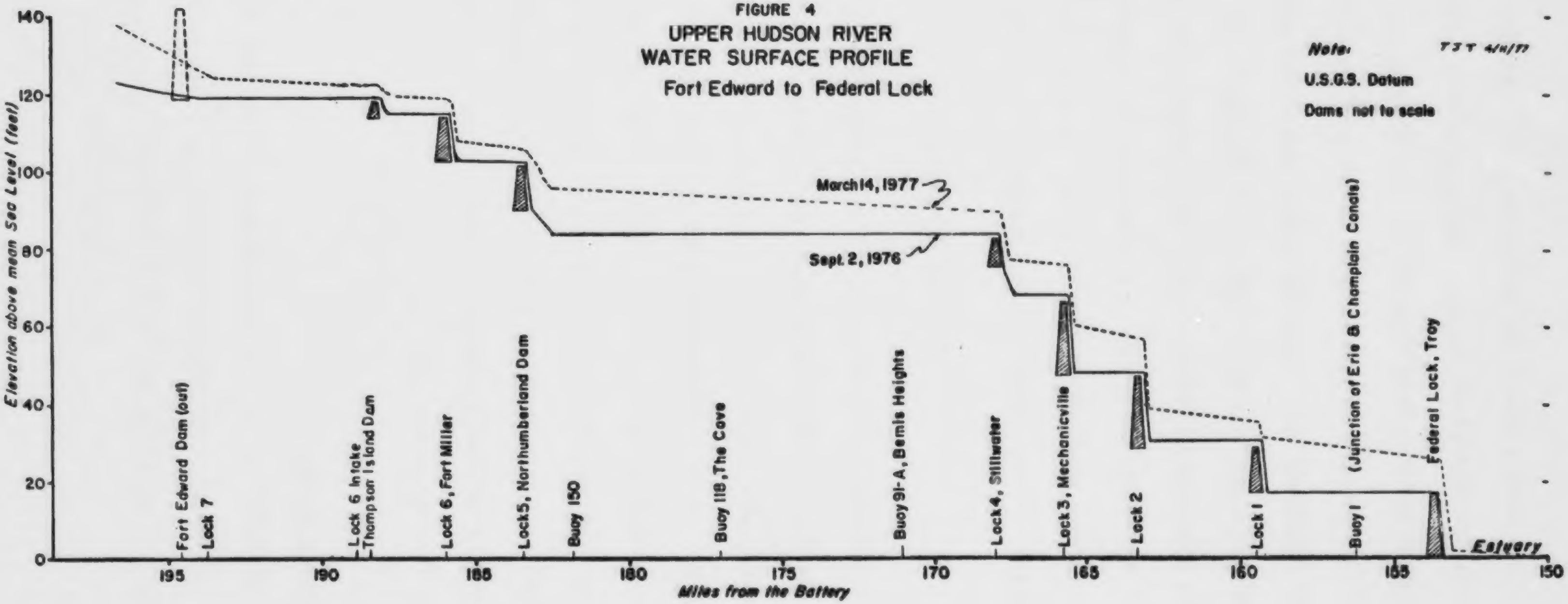

N
WARREN CO.
SARATOGA CO.
(11-04)
#1-3180
#1-3280
LUZERNE
HADLEY
SACANDAGA RIVER
220
CORINTH
PALMER FALLS DAMS
SPIER FALLS DAM
210
SHERMAN ISLAND DAM
200
DIVERSION
WASHINGTON CO.
WARREN CO.
GLENS FALLS
DAMS
FEEDER DAM
HUDSON FALLS
#1-3275
CHAMPLAIN CANAL DIVERSION
FORT EDWARD
LOCK #7
DAM (REMOVED 1974)
190
DAM
DAM, LOCK #6
DAM LOCK #5
RIVER
SNOOK KILL
SCHUYLERVILLE
BATTEN KILL
(11-03)
180
KAYADEROSSERAS CREEK
SARATOGA SPRINGS
SPRING RUN
FISH CREEK
SARATOGA LAKE
GLOWEGEE CREEK
#1-3306
#1-3300 (DISCONTINUED)
BALLSTON SPA
HUDSON
170
STILLWATER
WASHINGTON CO.
RENSSELAER CO.
BALLSTON CR.
ROUND LAKE
DAM LOCK #3
ANTHONY KILL
DAM, LOCK #4
#1-3357 (P.R.)
MECHANICVILLE
HOOSIC RIVER
(11-02)
#1-3355 (INACTIVE)
DWAAS KILL
DAM LOCK #2
#1-3575
160
0 1 5 10
SCALE: MILES
DAM LOCK, #1
MOHAWK RIVER
WATERFORD
SARATOGA CO.
ALBANY CO.
COHOES
#1-3580
WATERVLIET
TROY
LEGEND
MILE POINT
U.S.G.S. GAGE

UPPER HUDSON RIVER BASIN

FIGURE 3

FIGURE 4

UPPER HUDSON RIVER
WATER SURFACE PROFILE
Fort Edward to Federal Lock



Note:
U.S.G.S. Datum
Dams not to scale

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downriver has been removed by Department of Transportation's (DOT) dredging to maintain the Champlain Canal. Much, however, still remains, particularly in the region between Fort Edward and the Thompson Island dam.

The essence of the Hudson River problem is that these PCBs are now slowly leaching back into the river and if no action is taken, may continue contaminating the river and its biological system far into the future. It is also possible, however, that the contaminated sediments may be covered or moved by nature to a section of the river where they may no longer present a problem or that they may have so spread out over the entire length of the river that no action is possible.

THE PLAN OF STUDY

Although research prior to and since the court proceedings demonstrates a serious problem does exist with respect to PCBs in the Hudson River, the complete scope of the problem and the appropriate remedial action are not clear. The State plan adopted is a complex program to ascertain the seriousness and precise location of PCB contamination in the Hudson River and to evaluate the cost, environmental as well as financial, of any remedial action. This program has been formulated by DEC, approved by the Advisory Committee, and is now underway (Figure 5). A summary of this plan follows

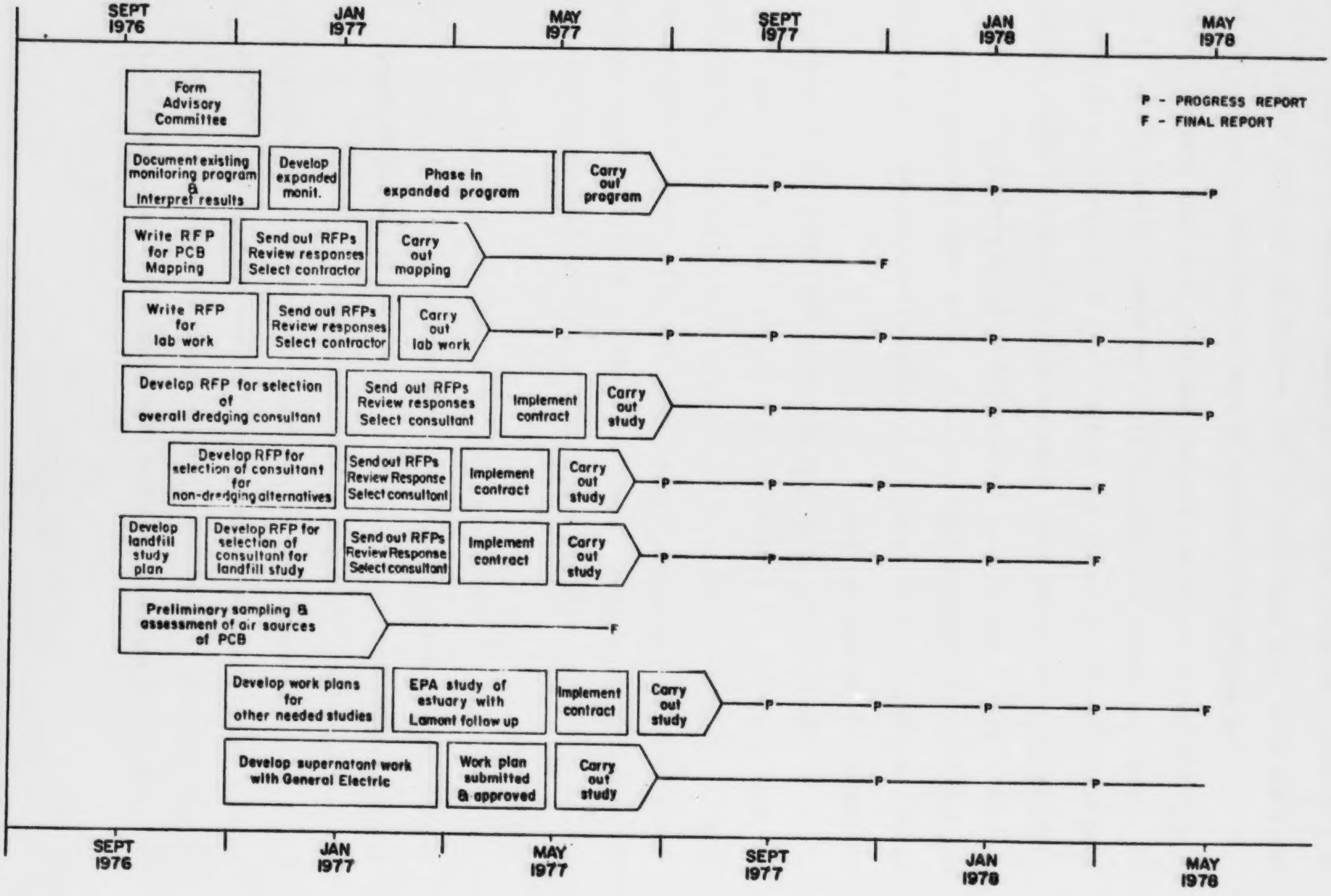
A. Monitoring Study

In order to define the concentrations and movements of PCBs in the river system, a comprehensive monitoring program has been developed. The program(11) outlined in Table 3 includes monitoring of fish, macro-

FIGURE 5

PLAN FOR IMPLEMENTATION OF PCB SETTLEMENT

MAY 1977



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invertebrates, sediment, hydrology, wastewater treatment plant input, water and air. Some highlights of this program are described below.

The Department's Division of Fish and Wildlife is responsible for a basic biological monitoring program, and as part of this program, it will be collecting fish at six sampling locations spread throughout the river from Stillwater to the Tappan Zee Bridge. Most of the sampling will take place in the Lower Hudson River where commercial fishing interests are the greatest. Nine common species are expected to be sampled, mostly during May and June, but American Shad were taken during their spawning run in April. In addition to these studies, macroinvertebrates are being sampled throughout the spring and summer.

These animals, as well as all other materials, will be analyzed for PCBs by chemists at O'Brien and Gere Engineers of Syracuse, New York. This firm follows a rigorous quality control program designed and monitored by the Department of Health and can handle the large number of samples expected during the program. Before the study is complete, several thousand samples will be analyzed for PCBs using a gas chromatograph-electron capture detection.

Normandeau Associates, Inc. of Bedford, New Hampshire, was awarded a contract to map the river bottom measuring the sediment thickness and PCB content from Fort Edward to the Troy dam, in the region where sediment was shown to be most heavily contaminated.

In December 1976, the EPA Region II office used a helicopter to collect Hudson River sediments between Troy and the Tappan Zee Bridge because sampling in this region had previously been scanty. Results of this survey (12) suggested that the Lower Hudson River also has highly contaminated sediment in at least four of the twenty sites sampled. To further investigate this possible problem, a contract is in process with Lamont Doherty Geological Laboratory. Lamont Laboratory has collected, analyzed and archived cores in the Lower Hudson over the past several years. With this unique collection and new ones from selected sites, it should be possible to get a much better understanding of PCB levels throughout the estuary portion of the Hudson River.

The United States Geological Survey is cooperating in the study by continuing their work on sediment transport, particularly during big storms and the spring thaw. Because high water in the river often moves large volumes of sediment, PCB measurements provide an indication of whether, and how rapidly, contaminated sediments in the Upper Hudson move downriver.

Not included as part of the program, but a study that will contribute to it, is an aquatic ecology and water quality study being done by Equitable Environmental Health, Inc. for Niagara Mohawk Power Corp.(13) as input to their preparation of an environmental impact statement for possible reconstruction of a hydraulic dam at Fort Edward.

B. Need for Active Restoration

All of this new information, and the previously collected data, will be synthesized and analyzed by three different teams of scientists and engineers. Two of these teams have been commissioned to study the fate of PCBs in the river if no action is taken to remove them. The first, the firm of Lawler, Matusky and Skelly of Tappan, New York, will concentrate on PCB contaminants in the sediments and their movement in the river. The second, Hydroscience Associates, Inc. of Westwood, New Jersey, will concentrate its efforts on the biological systems and PCB uptake from the water and sediments.

The third team is Malcolm Pirnie, Inc. from White Plains, New York, who has been awarded a contract to determine the technical feasibility, engineering methodology, cost and environmental impact of dredging contaminated sediments from the river. Although many other methods have been suggested for removing PCBs from the river, at the present moment, dredging is the only proven technology which could be applied in the immediate future. Other techniques would probably take at least five years before they could be used on the necessary scale. By then, the highly contaminated, and presumably confined, sediments might well be elsewhere.

Additional information on dredging of PCB contaminated sediments will be gained as a result of dredging operations planned for the summer of 1977(6,7). Although the primary purpose of this operation is maintenance of the canal system in the Fort Edward area, the work will be closely monitored in order to evaluate the practicality of dredging in PCB contaminated areas.

Dovetailing with Malcolm Pirnie's work, Weston Environmental Consultants of West Chester, Pennsylvania, are evaluating various landfills and dredge material disposal sites. If dredging is to be seriously considered, the dredged materials must be treated and/or placed somewhere. Leaching could return much of the PCBs back to the river unless adequate precautions are taken.

The results of these studies are due early in 1978. Hopefully, they will provide the basis for deciding whether remedial action is desirable. If dredging is the proper action to be taken, how, when and where should it be done to provide the greatest removal with the least environmental impact and least cost? If it appears that dredging is unwise, then what direction should DEC take in attempting to solve this problem? The answers to these questions will not be simple but the work being carried out as part of the PCB settlement will insure that in making them we will have the best scientific input possible.

A multitude of geologists, chemists, biologists and engineers from State and Federal agencies, private firms and educational institutions are directly involved in this massive study. A list of the principal groups involved is given in Table 3. Such a cooperative endeavor, although difficult, is becoming more commonplace as we realize the necessity of integrating our scientific and technological knowledge to solve problems of our own making. This study can be viewed as a test to see if such an effort can succeed.

Table 3

PCB-Hudson River Monitoring Program

Element	Description of Program	Being Carried out by
Hydrology	Several additional gaging stations have been established in the Upper Hudson River.	U.S.G.S.
Sediment	An extensive number of bed sediment core and grab samples are being taken in the Upper River to map the PCB contaminated areas. Some cores are being analyzed for radioactive Cesium-137 in order to date them.	Collections by Normandeau Assoc.; PCB analysis by O'Brien and Gere; Cesium-137 analyses by USGS.
	Several suspended sediment stations have been established to monitor movement of sediments and their PCB content.	U.S.G.S.
	A special study of bed-load sediment transport of PCBs is underway.	Rensselaer Polytechnic Inst.
	A screening survey of PCB concentrations in the Lower Hudson River has been completed.	EPA.
	A detailed follow-up study of the estuary sediments and their PCB concentrations is underway.	Lamont Doherty Geological Lab.
Groundwater	Limited groundwater samples are being taken as part of the study of landfills and dredge disposal sites and as part of a water supply program.	Roy F. Weston Assoc; DEC Div.of Pure Waters; Dept. of Health
Water column	Water column data will be collected regularly in the Upper Hudson River. Municipal water supplies using Hudson River water are being monitored regularly.	USGS; DEC Division of Pure Waters; DOH.
Fish	Fish will be collected at six sampling locations spread throughout the river from Stillwater to the Tappan Zee Bridge. Most of the sampling will take place in the Lower Hudson River where commercial fishing interests are the greatest.	Collection by DEC Division of Fish and Wildlife; analyses by O'Brien and Gere.
Macro-invertebrates	Macroinvertebrate samples will be collected at selected stations throughout the spring and summer.	Collected by DEC Div. of Pure Waters and Dept of Health; analyses by O'Brien and Gere.
Wastewater	A screening program of sewage treatment plant sludges is planned to determine which if any are potentially contributing significant quantities of PCBs to the river	Samples collected by DEC Div. of Pure Waters; analyzed by O'Brien and Gere.
Air	A sampling network of air quality has been set up in the Fort Edward area.	Samples collected by DEC Div. of Air Resources and analyzed by DOH.

Table 4
Estimate of Direct Expenses Related to GE/PCB Settlement
(September 1976 - March 1979)

Contract	Purpose	Amount Total	From GE PCB $
Normandeau	Surveying and mapping.	$ 98,686	$ 98,686
O'Brien and Gere	PCB laboratory analysis.	300,390	300,390
U.S. Geological Survey	Increased monitoring of PCBs, flow and sediments.	120,000*	60,000
Lawler, Matusky and Skelly	Study of no-action alternatives, with emphasis on sediment-PCB movement.	107,000	107,000
Hydroscience	Study of no-action alternatives, with emphasis on biological uptake of PCBs.	58,442	58,442
Malcolm Pirnie	Environmental Impact Statement for East Channel maintenance dredging; engineering analysis; preparation of plan and specifications; permit application.	75,000**	0
Malcolm Pirnie	Assessment of technology, cost and environmental impact of dredging PCB-contaminated sediments.	270,000	270,000
Roy F. Weston	Study of PCB landfill and spoil disposal sites.	225,000	225,000
Lamont-Doherty Geol. Laboratory	Track down sources of PCBs in Hudson estuary.	75,834	75,834
Rensselaer Polytechnic Inst.	PCB transport in Hudson River bedload sediments.	5,000***	0
Dr. Edward Horn	Coordinator of study and PCB Advisory Committee.	5,400	5,400
	Subtotal	$1,340,752	$1,200,752
Other Expenses			
Advisory Committee	Operating expenses.	25,000	20,000
Monitoring equipment and supply	Office and field equipment needed to carry out monitoring studies.	65,000	65,000
Project management	Special supplies and expenses related to project management.	19,248	19,248
New York State	In-kind services related to monitoring, data evaluation and study management.	250,000	00
	Total	$1,700,000	$1,305,000

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* $60,000 matching funds provided by USGS.

** Funded from Fort Edward Dam removal fund (NYS Legislative Appropriation, Chap. 992 of the Laws of 1974).

*** NYS Science and Technology Foundation.

Table 5

PCB Hudson River Settlement Budget Summary

General Electric Inhouse Research and Studies

Amount	Purpose	Status
$ 400,000	Research on environmental capability of its substitute non-PCB dielectric.	Work underway; interim report on substitute available(8).
400,000	Removal or treatment of PCBs in supernatant liquids and sediments from Hudson River sludge.	Work plan approved by Advisory Committee and Commissioner: work underway(9).
200,000	Research on effects on the environment of not more than three substances which may be hazardous to the environment.	Awaiting recommendation of Advisory Committee on selection of substances to be studied.
$1,000,000	Total Available.	

Department of Environmental Conservation River Reclamation Program

Amount	Purpose	Status
$ 800,000	Monitoring the presence and levels of PCBs in Hudson River waters in water, sediment, and biota (from Sept. 1976 to March 1978)*.	Monitoring study plan approved and work underway(11).
600,000	Studies related to remedial actions*.	Studies underway.
300,000	Management and miscellaneous expenses.	
1,000,000	Estimated future monitoring cost.	
3,300,000	Reserved for implementing remedial action.	
$6,000,000	Total Available ($3,000,000 from GE plus $3,000,000 from New York State).	

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*See Tables 3 and 4 for detailed breakdown.

If studies now underway indicate that no remedial action is advisable, or if required action will cost less than $3.3 million, the settlement specifies that the remaining funds will be utilized to aid in developing a program to regulate the storage and discharge of substances hazardous to the environment.

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Hudson River Sediment Distributions and Water Interactions Relative to PCB - Preliminary Indications*

Introduction

Substantial discharges of PCB to the Hudson River occurred for approximately 25 years near Ft. Edward and Hudson Falls, New York. Due to the recent construction of industrial treatment plants and in-plant changes to a substitute compound for PCB, these discharges of PCB to the Upper Hudson have been reduced to less than 1 gram per day. It is believed that much of the PCB became adsorbed on the sediment, wood chips and organic debris in the river.(1) In 1973, the Ft. Edward Dam was removed and much of the PCB laden sediment that had accumulated behind the dam washed downstream as bedload and suspended load. There were large dragline dredging projects in 1975 and again in 1977 near Ft. Edward to remove some of this material.(2) Several floods over the years have greatly spread out the PCB laden sediment. Routine channel dredging for many miles downstream of Ft. Edward has removed some additional PCB. Barge traffic in the river may have contributed to spreading out of the PCB laden sediment. Extraction of PCB from the sediment to the water and volatilization of PCB from the water may have reduced the PCB concentrations in the first couple inches of bed sediment. Biological degradation and dilution of the PCB laden sediment may have had a similar effect.

Methods

Roughly 700 grab samples and 250 cores of the bed sediment and 25 bedload samples were taken in the Upper Hudson over a 40 mile river reach from Ft. Edward to Troy, New York(3). Bedload samples were taken with the Bogardi T-3 and Helley Smith samplers.(4) The cores averaged 14 inches (35 cm) in length and were typically cut into 4 sections. However, some cores were as long as 5 ft.(1.8 m) and were sectioned every inch.

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*T.J. Tofflemire, N.Y.S. Dept. of Environmental Conservation, Albany, N.Y. and T.F. Zimmie, Civil Engineering Dept., Rensselaer Polytechnic Institute, Troy, N.Y.

Analyses on these sediments included grain size, volatile solids, and PCB on most of the samples. PCB was always reported as 3 aroclors 1016, 1221, and 1254 and the total. Some of the sediments were subjected to 16 hour soxlet extraction and some to 1 hour shaker extraction. Many of these samples were not yet analyzed for PCB at the time this paper was written. Therefore, the data indications are preliminary and subject to change as more data becomes available. A lesser number of sediments indicated in Table 1 and 2(5) were analyzed in 1976 for dry bulk density, floatable solids, and total extractables (oil and grease). Some samples were examined under a binocular microscope by a geologist and also subjected to energy dispersive x-ray analysis using a scanning electron microscope.(5)

Sediments were collected as indicated in Table 1 and placed in clean 1 quart glass jars with an aluminum foil seal, which were stored at 5°C until use or analysis. Some sediments were dried at 60°C and dry sieved through clean brass sieves according to standard soil testing procedures. Suspended solids, % solids and % volatile solids were done in accordance with "Standard Methods for the examination of water and wastewater",(APHA) 13th edition. Turbidity was done with a Hach D.R. Engineers Laboratory kit (nephalometric type instrument). Floatable solids was done as follows: The sediments were dried at 100°C, weighed, placed in a known weight of water and stirred for 1 minute. The floatable matter was removed with a spatula. The weight loss due to removing the floatable matter was determined and dividied by the dry weight of sediment used to get % floatable. By this procedure some adsorbed water was removed in the floatable matter.

Water samples for PCB analysis were collected in hexane washed glass bottles with ground glass stoppers. Water and sediment samples were analyzed for the three arochlors of PCB by standard procedures used by the N.Y.S. Dept. of Health, Albany, and adopted by O'Brien and Gere Engineers, Syracuse. If not otherwise stated, total PCB is used.

For the sediment water mixing studies, 4 liter beakers and a standard four position gang stirrer were used. Sediments of known moisture contents were weighted wet and the proper dry sediment to Hudson River water weight ratios obtained to simulate dredging conditions. A total solution volume of about 2.8 liters was used per beaker. Parameters varied in the 13 jar tests included mixing time, settling time, sediment to water ratio, and sediment PCB concentration. It was also decided to determine both soluble desorbed PCB and total PCB including that in the suspended solids as desired. To separate the solids from the liquid, an International Model PR2 centrifuge was used at 3300 rpm and 2000 RCF. The wet solids were transferred to an extraction thimble and filtered therein. The liquid was put back in the centrate. The solids in the thimbles were analyzed as sediment samples. Centrifuging was not sufficient to effect complete solids separations. Therefore, 3 samples that had been centrifuged were split and ½ filtered through a .45 µ millipore filter. The filtered solids were also placed in the extraction thimble. Then the liquid samples were submitted for PCB analysis according to standard procedures. For some of the water samples an emulsion formed, but it was broken by adding and wasting methanal. On the samples were an emulsion occurred, 3 to 4 extractions with hexane, as opposed to the normal 2 extractions were performed, to remove essentially all the PCB.

In addition, many 500 ml jar tests on 20 different polymers and chemicals were conducted to determine the best coagulent for removing turbidity rapidly from sediment water mixtures.(6)

Full scale dredging with cutterhead hydraulic dredge(figure 3) operated by the N.Y.S. Department of Transportation was monitored at 3 sites. (A) Lock 1, 3 miles north of Waterford, N.Y. (B) Bouy 212, 3 miles south of Ft. Edward, N.Y. and (C)Lock 4 near Stillwater, N.Y. The dredge pumped about 20-24 cfs(34-41 cu m/ min.to individual spoils lagoon areas where most of the solids settled and the water returned to the river through a wood overflow box structure. The return flow was monitored daily and samples periodically taken for turbidity, suspended solids, PCB and heavy metals.

Polymers were fed on the dredge to improve the turbidity removal in the spoils lagoon. They were fed by a Cole Palmer masterflex pump into a line receiving tap water dilution and then into the suction side of the dredge pump. The polymers mixed with the dredged slurry in the pipeline. The velocity in the pipeline was 20 ft/sec(7.1 m/s). At Lock 1, three different cationic polymers Drew Floc 410, Nalco 7134 and Calgon Cat floc B were tried in 2-8 hour experiments on 3 different days. At Bouy 212 Cat floc B was fed continuously after 9:30 a.m. for almost every day of dredging. At Lock 4, Cat floc B was additionally fed at the second stage of a 3-stage lagoon system through a gravity pipe diffuser.

Salt tracer studies were performed to determine the retention times of the spoils lagoons. A 100 lb(45 kg) bag of calcium chloride was dumped at the pipe entering the lagoon and the conductivity monitored at the overflow box structure. Styrofoam chips were dumped and timed to also give approximate flow through times.

Bed Sediment and Bedload Data

The bed sediments typically contained wood chips, saw dust, shale chips, cinders, and coal fragments in the coarse sizes, while the fine sizes contained quartz and feldspar sand, fragments of the above, clay, muck and organic material(7). The fine fractions (less than .42 mm) usually contained much less wood. The bedload samples had similarlies to the bed sediment but generally contained less silt clay and muck. Figures 1 and 2 show sieved fractions of two bed sediments. Wood chips were noticed in the coarse fractions in Figure 2. Previous studies have noted the river bed is often fissible black shale of the Trenton group or Albany clays.

From the data in Table 2 and from microscopic examinations it was noted that wood chips were often present in the >.4 mm size fractions of bed samples but absent in the finer sizes. This contributed to often causing the coarser size fractions to have higher volatile solids and floatable solids and lower bulk density. For bed load samples, the wood was often present in the coarse sieve fractions but absent in the finer fractions. It is noted that saw dust is a good adsorber for oil and that PCB is oil soluble. The bedload from Waterford had considerably more round shale pebbles, while the up river samples contained more quartz and feldspar in the fine sands and more wood chips, angular shale chips and cinders in the coarse sizes(5).

For several typical samples that had wood chips, sand, and some muck, the PCB was present throughout all grain sizes. As indicated in Table 3, PCB was as high in concentration in the very coarse materials (>2 mm) as in the fine materials(<.075 mm). For some samples, the medium size sands were often lower in organics and PCB. From the analysis of about 1000 bed samples it was generally found that the highest PCB occurred in muck deposits high in volatile solids. However, some bed samples of coarse sand and wood chips were also moderately high in PCB. The analysis of this data is not yet complete however.

For 45 sieved bedload samples taken from the Waterford Rt. 4 Bridge in March 1977(Z01-49) there was a fairly good correlation of PCB and volatile solids, $r = .86$(4). It was also noted that some bedload samples taken at Ft. Edward and Schuylerville in March 1976 were high in volatile solids and PCB. However, the Waterford Rt. 4 Bridge bedload samples taken during high flow in March 1976 contained no wood chips, low organics and low PCB while some of the March 1977 samples at Waterford were higher in wood, organics and PCB. Table 4 summarizes the 1977 total calculated bedload movement appeared relatively small considering suspended load PCB movements of 5, 000

- 10,000 lb/yr (2270-4540 kg/yr) over the Troy Dam.(8) However, some of the PCB concentrations in the bedload were surprisingly high, 80 ppm for example on 4/1/77. The bedload may have been higher in an open river without dams.

Figure 4 provides a hydraulic profile of the Upper Hudson and indicates the eight dams(7 river reaches) from Ft. Edward to Troy. Although all analyses on the 700 grabs and 250 cores are not all complete, preliminary indications are that the highest PCB concentrations were in the first river reach with values over 1000 ppm behind the Thompson Island Dam. Concentrations of 25-100 ppm in this upper river reach were common while the lowest river reach(Lock 1 to Troy Dam) had concentrations of 5-25 ppm. In the river, it was noted that the muck deposits typically occurred along the banks and the coarse sands in the main channel. Malcolm Pirnie Inc.(10) found that the mean of the 700 grab sample D50 sizes was about .3 mm. The D50 is the sieve size that passes 50% of the sample. In addition,20% of the samples had a D50 of greater than 2 mm while another 10% of the samples had a D50 of less than .06 mm(the silt size division).

The 250 cores from the Upper Hudson and their 1000 to 1200 subsections were only partially analyzed at this writing. However, there did appear to be a trend of the PCB being highest in the layer 3-8"(7.6 -20 cm) below the top of the core. Generally the PCB did not extend below 2 ft. (.6 m) in the core, although there were exceptions to this. Many of the cores were taken near the river banks where muck deposits were most prevalent.

Sediment Water Interactions

As described in more detail in another report(5), 13, 2.8 liter jar tests were performed in which Hudson River sediment was mixed with clean river water in usually 1/10 sediment to water ratios. After various settling times after various solids separation procedures(centrifugation or filtration) PCB, suspended solids, and turbidity were measured in the water and in the fine solids separated from the water. The sediment total PCB generally ranged from 10-300 ppm and caused a total water PCB of 10 to 200 ppb and a soluble water PCB of 2-6 ppb. This gave a sediment to soluble water PCB partition coefficient ranging between 10^3 and 10^5 and typically near 10^4 for mixed jar tests simulating dredging. For a river situation simulated by a fish tank experiment with water flowing over sediment in a tank, the partition coefficient appeared closer to 10^5.(5) Diffusion of the PCB off the bottom and into the entire water column may add a limiting factor here since soluble PCB values for Upper Hudson River water are typically less than .5 ppb. Elutriate tests on Hudson River sediment authorized by N.Y.S. Department of Transportation also confirmed soluble water PCB concentrations in the 2-6 ppb range.(6) However, a few jar tests on sediments high in PCB and volatile solids indicated some unusually high soluble PCB values of about 50-100 ppb.(5) It is not yet known what the cause of this was. However, it may have been due to a fine suspended turbidity or to a high level of soluble oils and TOC in the water or due to a scum accumulation on the water surface which was included in the water sample tested for PCB. Jar tests on Hudson River sediments by Malcolm Pirnie(9) provided some other usefull insights. As the water to sediment ratio increased from 10/1 to 10,000/1 there was a 30-40 fold increase in the total quantity of PCB suspended or extracted from a given weight of PCB in the sediment. This implies that higher river flows will extract more total pounds of PCB from the river bed and at the same time yield a higher partitioning coefficient.

The data from the 13 jar tests were plotted in Figure 5 and related PCB and suspended solids in the water. The PCB values and other data on the T01 sediment were given in Tables 2 and 3. The T01 sediment PCB was 26.45 ppm while the less than .075 mm size fraction had a PCB of 35.55 ppm.

It is possible that the sediment fines suspended in the jar water after several hours were much smaller than .075 mm and had a PCB content of 100 ppm. If this is assumed, then the PCB in the water can be calculated directly from the suspended solids in the water as noted in Figure 6 for T01 sediment. Correlating the PCB and suspended solids data in Figure 5, gave an r-value of .76. In a jar test, it appeared that PCB in the sediment was extracted to the partition coefficient level in the water in less than one hour.

Many additional 500 ml jar tests were conducted on Hudson River sediments in which only turbidity and frequently suspended solids were measured (6). Some of these are summarized in Table 5. It was found that sediment high in volatile solids and in silt and clay caused high water turbidity and suspended solids that did not settle quickly. The addition of a 20 mg/l cationic polymer or 100 to 180 mg/l of alum followed by 1.5 to 2.5 hrs. of settling gave turbidities $<$50 JTU, and suspended solids $<$50 mg/l. The rapid mix time was usually 1 min., while the flocculation period was 4 min. For some sediments the turbidity coagulated, flocculated and settled with the aid of cationic polymers in 15 minutes. For other sediments the flocculation period with polymer was critical and a 1 minute rapid mix and 1 min. flocculation gave poorer results than a 4 min. flocculation time when equal settling times of 1½ to 2½ hours were employed. About 20 different cationic and anionic polymers were tested in various dosages and three cationics Drew floc 410, Nalco 7134 and Calgon Cat floc B were found most effective. The polymer had a cost of 30-40 ¢/lb. which was 5.0-6.6 ¢/1000 gal. at 20 mg/l.

In the jar tests, heavy metals were also measured and it was found that lead, and occasionally chromium were high relative to the return water standard. For some of the mucky sediments, iron was very high and caused a red color in the water.

Full Scale Dredging Data

The N.Y.S. Department of Transportation hydraulic dredge shown in Figure 3 was monitored at 3 sites on the Upper Hudson-Lock 1, Bouy 212, and Lock 4. The Lock 1 spoils lagoon was on a small island that had a fractured shale bottom. The lagoon walls or dikes were also made of shale chips and sand. For the first month of pumping at 20-24 cfs(34-41 cu m/min) into the lagoon, there was almost no effluent over the spillway box leaving the lagoon. The dredging water filtered through the dike walls and bottom and returned to the river. This water was sampled on several occasions and found to have quite low turbidity($<$ 20JTU).

The rocks settled in the influent end of the lagoon as shown in Figure 6, and the fines near the effluent end of the lagoon. The lagoon retention time was about 15 minutes, and some short circuiting of the effluent out the typical box shown in Figure 6 occurred. As indicated in Table 6, the combination of four factors-(A) 26% silt and clay in the sediment dredged,(B) only 1% solids on the average pumped by the dredge,(C) short retention time of 15 minutes and (D) 15 ppm of total PCB in the sediment being pumped-resulted in only 80% removal of suspended solids and 73% removal of PCB. When 15-20 mg/1 of cationic polymer was temporarily fed on the dredge, these removals increased to 96% for suspended solids and 95% for PCB. However, with the short retention time some of the flocculated sediment fines were flushed and scoured out of the lagoon upon dredge start up.

The Bouy 212 spoils lagoon site was on a silty loam soil and had deep, well compacted dikes near the river bank. There was much less percolation here. Figure 7 shows a portion of the dikes with sediment accumulated and the lagoon drained. Wood chips and sand were the dominant materials dredged.

A drag line shown in the background was used to pull accumulated sediment out of the lagoon so that its limited volume was not filled up with sediment. As noted in Figure 8 an oil boom was used to retain the scum which was found extremely high in PCB (18,000 ppm dry wt). The scum was partially removed by raking it up onto the dikes. In the future a better scum removal system is recommended. The sediment dredged had about 5%, the retention time was about 45 minutes and the sediment PCB was about 100 ppm. Cat floc B was fed on the dredge most of the time. Typical removals were 99% for suspended solids and PCB. The polymer cut the effluent suspended solids and PCB about in half as noted in Table 6. For both sites it was likely that there was only about a 5% increase in the downstream river concentration of PCB due to the dredging return flow. Sampling of the river upstream and downstream of the dredge indicated that the loss of sediment due to dredge head disturbance was minimal. Additional discussions of these two sites (Lock 1 and Bouy 212) are available (6, 11, 12).

The Lock 4 spoils lagoon was also on an island of fractured shale and there was considerable seepage through the bottom and sides which was observed to be clear and have a turbidity of less than 20 JTU. Figures 9 and 10 show the Lock 4 site which initially had 2 lagoons in series and later 3 lagoons in series. The last lagoon was long and narrow. It had brush and tall grass and roughly a 30 minute retention at peak flow. An oil boom was used to retain the scum which developed Cat floc B at 20 mg/l was periodically fed on the dredge or to the effluent box before the last lagoon. When the polymer was fed on the dredge, turbidity and suspended solids values were usually cut in half. When polymer was fed at the last box, turbidity values were dramatically reduced to less than 10 JTU as opposed to no polymer values of over 500 JTU.

It is felt that excellent flocculation and mixing occurred as the effluent passed through the long narrow channel with brush. In addition, the polymer was not wasted by attachment to sand which settled in any event in the first lagoon. Some preliminary data on Lock 4 is given in Table 6. The PCB results were not yet available.

It was also observed at this site that at a retention time of 15 minutes or less there was a flushing of fines out of the first lagoon upon dredge start up. More details on the Lock 4 dredging and on intensive river monitoring near the dredge head are available (13).

Summary Indications

Bed Sediment:

The sediment from the Upper Hudson was typically a mix of wood chips, organic debris, cinders, coal fragments, shale chips and sands, especially in the main channel. The muck and silt deposits were generally along the banks and occasionally very high in PCB. The PCB was not all in the fine material, but also in the coarse material. Frequently the PCB concentrations in the most contaminated cores were highest in the 3-8 inch(7.6-20 cm) layer below the top.

Bed Load:

At Waterford, there was a good correlation between PCB and volatile solids in the bed load. The bed load was a relatively small percentage of the total suspended load PCB transport. There appears to be an increase in the wood chips, volatile solids and PCB in the bed load at Waterford from April 1976 to March 1977.

Sediment-Water Interactions:

From jar tests simulating dredging, the partition coefficient between soluble PCB in the water and in the sediment was 10^3 to 10^5. This coefficient increased as the water to sediment ratio increased. In jar tests on various Upper Hudson sediments, the reduction of turbidity and suspended solids in the water resultedin reduction of PCB and heavy metals in the water. Cationic polymers were effective in rapidly reducing the turbidity in the sediment water mixtures.

Dredging Experience:

In summary, it was observed that the removals of turbidity and suspended solids in the dredging water mixture was a function of lagoon retention time, polymer feed and the nature of the sediment dredged (% silt and clay, and % volatile solids). It was found that:

1. A retention time of one hour in the spoils lagoon is the first step of best practical treatment to assure at least 90% removal of suspended solids. For coarse textured sediments with low % volatiles, the removals may be greater. Jar tests on the sediment water mixtures of the sediments to be dredged are the simplest way of testing this in advance for a given site. In rivers such as the Hudson, which often have a velocity of 1 fps, the elutriate test which measures only soluble pollutants, gives only part of the information needed.

2. To achieve one hour flow through time as measured roughly by the time from the addition of salt at the lagoon influent to the time of the peak of the conductivity at the lagoon effluent, one of several steps must be taken.

   A. The lagoon must be greatly oversized initially if no changes in the lagoon are to be made during operation, or

   B. The lagoon must have sufficient depth so that the water level can be periodically raised as the sediment fills in the lagoon volume, or

   C. Heavy equipment must be frequently used in the lagoon to remove accumulated sediment.

3. Longer retention times (1 hr. to 18½ hrs.) are encouraged and will probably give suspended solids removals of 95-99%. At long retention times, it is doubtful that the cost of the polymer will be worth the results achieved.

4. 20 mg/l of cationic polymers, Nalco 7134, Cat floc B, and Drew floc 410 were found very effective in coagulating and flocculating turbidity in the dredging lagoon. They were most beneficial in reducing suspended solids when the retention time was less than 30 minutes. Retention times of 30-15 minutes with polymer may achieve almost a good a removal of suspended as 1-2 hours with no polymer. Retention times of less than 15 minutes frequently five suspended solids removals of no greater than 80% and should be basis of shutdown of dredging

until changes are made. Upon dredge start-up at 15 mins. lagoon retention, there is often a large flushing of sediment fines out of the lagoon.

5. The polymer is most effective when fed in the second stage of a two-stage lagoon system. Good mixing and flocculation of the polymer is essential to improve its effectiveness. Good mixing and flocculation is sometimes difficult to achieve when the polymer is added between lagoons. In such a case, it may be better to add the polymer on the dredge and benefit from the mixing in the pipeline. Alum proved as effective as cationic polymer in jar tests and is considerably cheaper. However, the large volumes to be fed and sludge production are problems with alum.

6. Chlorocarbons and PCB tend to concentrate in a scum or oil layer which accumulates on the surface of some dredging lagoons. This scum layer should be periodically removed from the top of the lagoon and buried or disposed of properly. An oil boom is the first step to retain the scum, but a method of removal such as a gravity scum drain-off must also be planned for and built into the lagoon system.

7. Permeable sand or shale lagoon dikes provide very effective suspended solids removal and will lengthen the retention time in the lagoon. However, pollution of present or ptential well waters must be avoided.

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Table 1. HUDSON RIVER SAMPLES AND LOCATIONS

Old Number	Date Reanalyzed	New Number	Date Collected	Access. Number	Location and Mile Point	Method	Visual Comment@
Bed Samples							
11 PCB 113	3/17/76	11 PCB T06	9/5/75*	See Table 2	Near Waterford- W. Bank, 1½ mile upstream from Alb. Co. Line M.P. 157.6	shovel	silt, sand
11 PCB 603	3/17/76	11 PCB 603	8/27/75	-	Hudson Falls (V), upstream of Baker's Falls Br., M.P. 197.3 , N.W. shore	shovel	org. sand
11 PCB 611	3/17/76	11 PCB 611	8/27/75	-	Northumberland - N.E. shore at Rte. 4 Br. - M.P. 183.5	hand	org. silt
5363	3/17/76	11 PCB T08	8/14/75	01691	Ft. Edward, west channel below railroad bridge	backhoe	clay - 2-4' deep
11 PCB 606	3/17/76	11 PCB T07	8/27/75	See Table 2	Fort Edward,N.E. shore at D & H railroad bridge - 194.2	hand	org. silt
		*11 PCB T01	2/24/76	00068, See Table 2	Rt. 4 bridge near Northumberland, M.P. 183.5	dredge	sandy
		*11 PCB T02	3/2/76	00072	Champlain canal at 200 yds so.of Guard gate	shovel	sandy with rocks
		***11 PCB T03	3/10/76	02096	0.35 mile below Lock #1, M.P. 159.0 Boat sample in canal channel	dredge	
		11 PCB 150	3/9/76	01627	Off Rt. 29 bridge 100' from west shore, Schuylerville, M.P. 181.2	dredge	sand & silt, dark
		11 PCB 151	3/9/76	01628	3' off west bank at Fisherman's Rest Marina, Saratoga (T), M.P. 177.4	shovel	silty sand, dark
		11 PCB 152	3/9/76	01629	Off shore at no. end of River Road across from pk., Stillwater (T), M.P. 174.2	dredge	sand, clean
		11 PCB 153	3/9/76	01630	From dock on Ferry Rd., 1200' north of Rt. 67 bridge, Stillwater (V), M.P. 168.4	dredge	sand
		11 PCB 154	3/9/76	01631	From Mechanicville, Hemstreet Park bridge, M.P. 165.3	dredge	sand

TABLE 1. - Continued

Old Number	Date Reanalyzed	New Number	Date Collected	Access. Number	Location and Mile Point	Method	Visual Comment@
		11 PCB 155	3/9/76	01632	Off north end of Lock 1 Bullnose Halfmoon (T), M.P. 159.0	dredge	silty sand
		11 PCB 156	3/9/76	01633	5' off west shore 300' south of bridge, Waterford (V), M.P. 156.5	shovel	org. silt
11 PCB 801	3/17/76	--	9/30/75	See Table 2	Above Thompson Island dam, M.P. 188.4	core	See Table 2
BedLoad Samples 11 PCB T10							
		Z01	3/23/76	02257	Rt 197 East Bridge, Ft. Edward	Bogardi	Z10 high flow ↑
		Z02	3/23/76	02010	Rt 197 East Bridge, Ft. Edward	"	Angular Rocks
		Z03	3/23/76	02097	Rt 197 West Bridge, Ft. Edward	"	Z09 high flow
		Z04	3/23/76		Rt 197 West Bridge, Ft. Edward	"	
		Z05	3/24/76	02098	Rt 4 Bridge, Northumberland	"	
		Z06	3/24/76	02099	Lock 5 Bridge, Schuylerville	"	
		Z07	3/24/76		Rt 29, East Bridge, Schuylerville	"	
		Z08	3/24/76	02100	Rt 29 Bridge, West, Schuylerville	"	Z11 high flow ↓
		Z13,212	4/2/76		Waterford Bridge, high flow	"	Round roc coarse
Water Samples							
		*11 PCB T04	3/15/76	01679	Corinth, Rt 197 bridge, WQSN site M.P. 214.9	grab	Turb.= 9
		**11 PCB T05	3/15/76	01950	Ft. Edward, city dock in village WQSN, M.P. 192.2	grab	Turb.= 19
		***		01949	Same as above, centrifuged to remove particulate	--	Turb.= 10

---

*Sample used for mixing studies with sediment.

**Centrifuge comparison samples.

***Sample used for a suspended solids vs turb. correlation.

@Unless otherwise noted, samples are the top 6-12" of sediment.

Table 1. Hudson River Samples and Locations

New Number	Date Collected	Access No.	Location	Method	Visual Comments
11PCBT100 (Buoy 214)	5/5/76	4063	Section at Buoy 214, .5 mi downstream from aerial cable.	dredge	sandy*
11PCBT103 (TI Dam)	5/5/76	4064	Section 100 yds above Thompson Island Dam	dredge	silty sand*
11PCBT101 (Buoy 200)	5/5/76	4065	Section at Buoy 200, 1000' North of Griffin Island.	dredge	sandy*

*See Table 6

TABLE 2. SUMMARY SEDIMENT ANALYSES

New No.	Ass. No.	Size Fract. mm	Wt % on Sieve	Volatile Solids %	Floatable Solids %	Comments	Total Wt Extracted ppm	PCB-ppm Total
11 PCB T01	0068	Total	100	6.0	9.0	62.5% solids	1029	20-40
dried 100°C		+2.0	10.1	25.76	57.0	Bulk density increased		
		+1.18	12.1	9.33	27.5	↓		
		+.595	37.6	5.94	9.8			
		+.420	17.2	1.59	.7			
		+.210	15.4	1.61	2.4			
		-.210	7.0	3.58	2.5			
11 PCB T01	1680	+2.0	12.0		23.8		2227	36.9
Resample	1681	+1.18	12.1		34.4		2958	36.1
	1682	+.59	32.1		12.7		862	41.1
dried 60°C	1683	+.42	15.5				94	4.85
	1684	+.21	19.0				550	5.75
	1685	+.075	7.1				1700	25.85
	1686	-.075	2.2				1680	35.55
11 PCB T02	0072	Total	100			54-41% solids TOC = 20% Tot N = .3%		4.5-13
		+2.0	70.0	1.68	3.4			
		+1.18	17.0	.94	1.1			
		+.595	7.1	2.63	6.6			
		+.21	3.2	4.66	7.2			
		-.21	2.6	2.76	5.1			
11 PCB T03	02096	Total	100	24.0	18.0	45.9% solids		3.3
		+1.18	11.9			Bulk density increased		
		+.42	21.0			↓		
		+.15	26.3					
		-.15	40.7					
11 PCB T06		Total	100	4.1	12.2	60.5% solids TOC = 3.4% Tot N = .2%		19.0**
	1690	+.42	13.5		14.0	Bulk density increased greatly	4731	34.6
	1689	+.15	50.2		2.7	↓	818	8.45
	1688	+.075	28.4		3.9		1090	3.6
	1687	-.075	8.0		11.16		3120	10.3
11 PCB T07		Total	100	6.3	37	35% solids TOC = 9.7% Tot N = .6%		233**
	1749	+1.18	6.4		98	Bulk density increased 4 fold	15500	671
	1748	+.42	15.3		75	↓	11474	257
	1747	+.15	38.5		33		3449	127
	1746	+.075	27.6		30*		2910	87
	1745	-.075	12.2		30*		5760	155
Bed Load Z03	02253	+.84	20.9	8.1			2230	135.8
	02252	+.25	63.2	1.27			901	13.35
	02251	-.25	15.9	.12			7587	3.35
Z08	02260	+.84	26.8	16.5			1536	65.7
	02259	+.42	36.4	1.82			811	8.4
	02258	-.42	36.8	.71	-		359	2.4

*Suspected to be high due to low test weight used.
**1975 PCB analyses

TABLE 2 (continued). SUMMARY SEDIMENT ANALYSES

New No.	Size Fract. mm	% Size <.074 mm	Volatile Solids %	Floatable Solids %	Comments		PCB ppm Total	Tot. Wt. Ext. ppm
11 PCB 603	Total	8.9	14.3	63.6			4.8	
11 PCB 611	"	14.1	9.9	68.6	Some wood chips		78.5	
11 PCB T08	"	50-90	2.7	0.0	Clay		.2	412
11 PCB 150	"	11.8	2.7	6.9	65.9% solids			
11 PCB 151	"	24.3	9.[illegible]	4.6	69.4% solids		.45	
11 PCB 152	"	4.8	1.1	0.2	Clean and dense sand, 77.6% S.		.55	
11 PCB 153	"	10.0	3.0	13.4	Light, 62.9% solids		5.2	
11 PCB 154	"	11.0	2.9	10.8	65.8% solids		2.6	
11 PCB 155	"	39.0	4.2	1.6	62.3% solids		2.35	
11 PCB 156	"	55.9	5.4	2.8	Light, 50.3% solids		5.95	
11 PCB 801					Relative Texture	Depth		
1	Total		8.1	15.4	Fine sand	1"	136	
2	"		9.4	17.3	Fine sand	2"	147	
3	"		3.9	10.1	Fine sand	3"	3707	
4	"		2.2	5.0	Coarse sand, dark	4"	1833	
5	"		13.2	20.4	Silty sand, light	5"	1211	
6	"		16.8	8.8	Silty sand, light	6"	617	
7a	"		5.9	9.1	Fine sand	7"	371	
7b	"		11.1	6.2	Silty sand			
11 PCB 10 - Bed Load Samples:								
Z01 - 02257	Total	.5	-		All sediment		14.3	449
Z02 - 02101	"	2.2	9.5		Some wood		36.5	3682
Z03 - 02097	"	.2	8.3		Some black flat rocks		20-37	2205
Z04	"	.2	8.9	36.8	Similar to Z03 and wood chips		-	-
Z05 - 02098	"	-	8.3				10.95	8860
Z06 - 02099	"	-	9.2				23.65	15029
Z08 - 02100	"	.3	5.5	2.5	Some black flat rocks and wood		22-30	725
Z07 -	"	.9			Some wood chips			
Z09 - 02933	"	.1	.7	.3			34.2	
Z10 - 02934	"	.9	9.9	34.1			27.5	
Z11 - 02935		.5	19.2	67.1	Many wood chips, some org.		116.[illegible]	

TABLE 3 - SEDIMENT SIZE FRACTIONATED PCB DATA*

I.D. No.	Size Fraction	Wt. %	PCB Conc. ppm 1221	PCB Conc. ppm 1016	PCB Conc. ppm 1254	PCB Conc. ppm Total	ppm of PCB in Total Sample 1221	ppm of PCB in Total Sample 1016	ppm of PCB in Total Sample 1254	ppm of PCB in Total Sample Total
11 PCB T01										
0068	Total	100%	3.3	16.0	.5	19.8				
1680	+2.0 mm	12.0	6.7	29	1.2	36.9	.804	3.48	.144	4.43
1681	+1.8	12.1	9.1	25.7	1.3	36.1	1.101	3.11	.157	4.37
1682	+.59	32.1	1.9	38	1.2	41.1	.610	12.20	.385	13.19
1683	+.42	15.5	<.1	4.4	.4	4.85	.008	.68	.062	.75
1684	+.27	19.0	<.1	5.0	.7	5.75	.010	.95	.133	1.09
1685	+.075	7.1	<.1	25	.8	25.85	.004	1.77	.057	1.84
1686	-.075	2.2	<.1	31	4.5	35.55	.001	.68	.099	.78
							2.538	22.87	1.037	26.45
11 PCB T06										
1690	+.42 mm	13.5	1.7	32.	.9	34.6	.230	4.320	.122	4.672
1689	+.15	50.2	<.1	8.0	.4	8.45	.025	4.016	.201	4.242
1688	+.075	28.4	1.2	2.2	.2	3.6	.341	.625	.057	1.022
1687	-.075	8.0	2.5	7.1	.7	10.3	.20	.568	.056	.824
							.796	9.529	.436	10.760
11 PCB T07										
1749	+1.18 mm	6.4	75	580	16	671	4.80	37.12	1.02	42.94
1748	+ .42	15.3	32	210	15	257	4.90	32.13	2.30	39.32
1747	+ .15	38.5	3.1	120	3.9	127	1.19	46.20	1.50	48.90
1746	+.075	27.6	13	69	5.0	87	3.59	19.04	1.38	24.01
1745	-.075	12.2	49	100	5.9	155	5.98	12.20	.72	18.90
							20.46	146.69	6.92	174.07
11 PCB T10-Z03										
2253	+.84 mm	20.9	39	95	1.8	135.8	8.15	19.86	.37	28.38
2252	+.25	63.2	<.1	13	0.3	13.35	.03	8.22	.19	8.44
2251	-.25	15.9	<.1	2.3	1.0	3.35	.01	.37	.16	.53
							8.19	28.45	.72	37.35
11 PCB T10-Z08										
2260	+.84 mm	26.8	5.7	34	26	65.7	1.52	9.11	6.97	17.60
2259	+.42	36.4	1.1	4.4	2.9	8.4	.40	1.60	1.06	3.05
2258	-.42	36.8	<.1	1.4	1.0	2.4	.02	.52	.37	.91
							1.94	11.23	8.40	21.56

*For values <.1 ppm, .05 ppm was used

TABLE 4

HUDSON RIVER BEDLOAD MOVEMENT

Date	Sample No.	Bridge on Hudson, Station	Approx. Flow-cfs	Total Bedload lb/day	Total PCB ppm	Total PCB lb/day
3/23/76	Z01	Fort Edward, East 230		904	14.3	.013
	Z02	Fort Edward, East 150		407	36.5	.015
	Z03	Fort Edward, West 250		6,512	28.5	.371
	Z04	Fort Edward, West 380		6,512		
						.399
3/24/76	Z05	Northumberland	9000	869	11	.010
	Z06	Schuylerville, Lock 5		36	23.7	.001
	Z07	Schuylerville, East 170		1,309		
	Z08	Schuylerville, West 110	9000	12,595	26	.330
4/2/76	Z09	Fort Edward, West 280	32,000	558,878	34.2	19.1
	Z10	Fort Edward, East 230		60,654	27.5	1.67
	Z11	Schuylerville, West 110		163,565	116.4	19.0
	Z12	Waterford Bridge, 110	49,000	62,700	16.0	1.0
	Z13	Waterford Bridge, 270		368,893	9.5	3.5
3/11/77	Z01 thru Z49	Waterford Bridge, 260	18,500	1,070	39.	.0418
3/14/77	and Z71, Z72	Waterford Bridge, 100, 470,260	54,100	86,318	6.1	.53
3/15/77	↓	Waterford Bridge, 260, 470	62,100	183,538	30.	5.55
3/16/77	↓	Waterford Bridge 260	45,700	14,976	4.81	.072
4/1/77	↓	Waterford Bridge 260	21,500	8,269	80.	.66

---

* Estimated

Table 6

Summary of Dredging Results at 2 Sites

	LOCK 1	BUOY 212	LOCK 4
LAGOON FLOW THRU TIME TYPICAL, BY SALT TRACER	15 min.	45 min.	55 min.
LAGOON INFLUENT			
Average % solids	1%	5%	3%
PCB in solids	15 ug/g	100 ug/g	
LAGOON EFFLUENT			
Suspended solids, without polymer	2000 mg/l	500 mg/l	460
Suspended solids, with polymer	400 mg/l	250 mg/l	230, 20*
PCB, composite, without polymer	40 ug/l	100 ug/l	
PCB, composite, with polymer	8 ug/l	50 ug/l	
REMOVAL EFFICIENCIES			
Suspended solids, without polymer	80%	99%	98%
Suspended solids, with polymer	96%	99.5%	99, 99.9*
PCB, without polymer	73%	98%	
PCB, with polymer	95%	99%	
SILT AND CLAY			
Percent passing #200 sieve (average)	26%	5%	20-30%

*Polymer fed between lagoons

Table 5

Summary of Jar Test Results Using Typical Hudson River Sediments

Sediment Location & Concentration	Float-ables %	Vola-tiles &	Silt & Clay %	For Settling Times 1.5-2.5 hrs.		For Settling Times 18-24 hrs.		For Chem. Coagulation*	
				Turb.	SS.	Turb.	SS.	Turb.	SS.
Schuylerville	9	6	2	1000	500	500	300	37	20
Ft. Miller	2	4	1	200	150	100	50	-	-
Buoy 214-Ft. Edward	2.7	2	11	800	450	500	200	45	20
Behind T.I. Dam	17.5	7	45	2500	1500	450	300	55	45
Stillwater	13.4	3	10	300	168	-	-	32	5
Lock 1 in canal	18	24	26	1150	715	162	94	-	-
Waterford Bridge	2.8	5.4	54	675	462	170	150	37	30

* 2½ hours settling

Figure 1, Sieved Bed Sediment at Lock 1 Dredging Site, June 1976

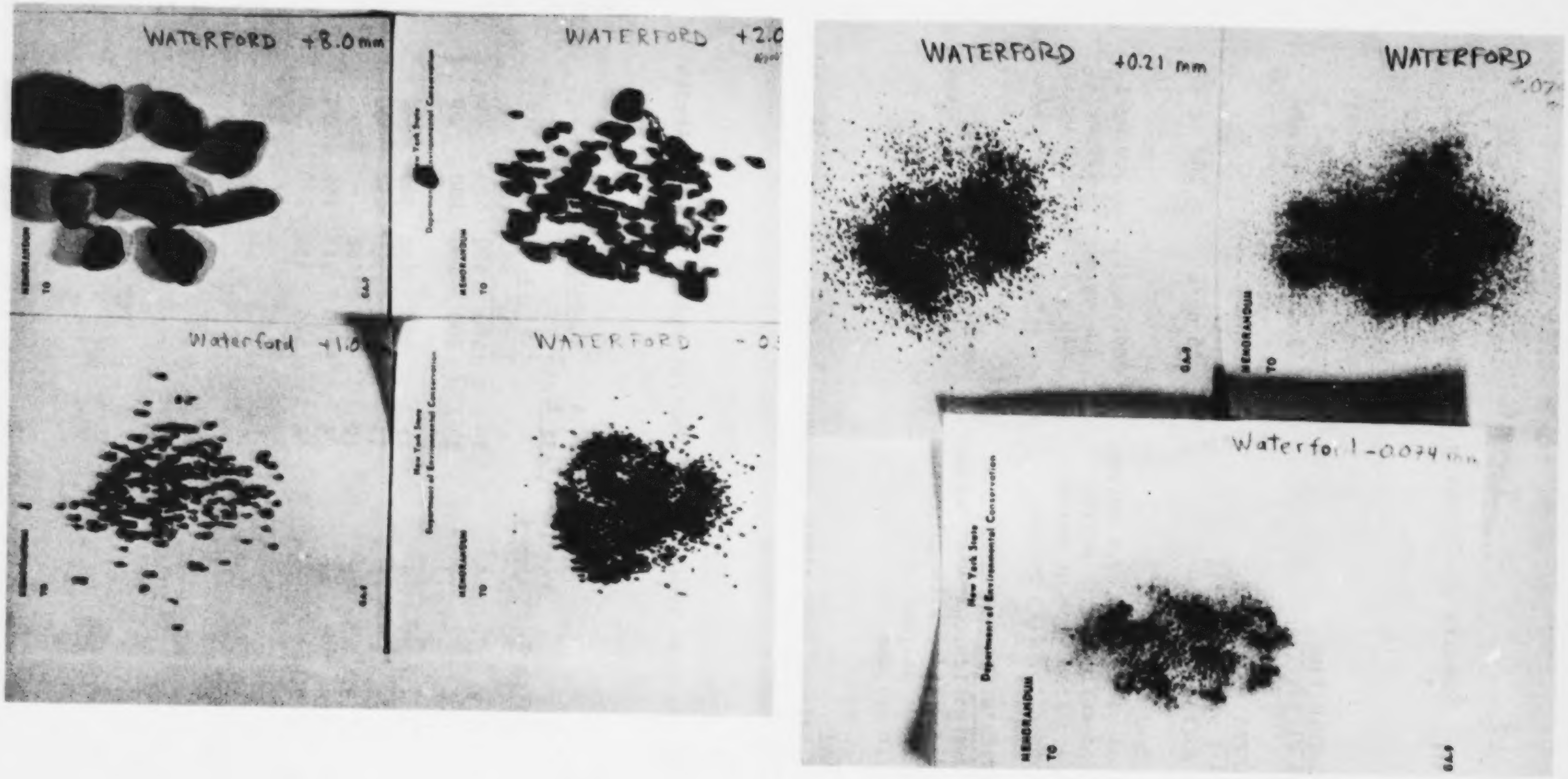

WATERFORD +8.0 mm
WATERFORD +2.0
Waterford +1.0
WATERFORD -0.
New York State Department of Environmental Conservation
MEMORANDUM
TO
WATERFORD +0.21 mm
WATERFORD
Waterford -0.074 mm

Figure 2 Sieved Bed Sediment at Bouy 212 Dredging Site, Oct. 1976

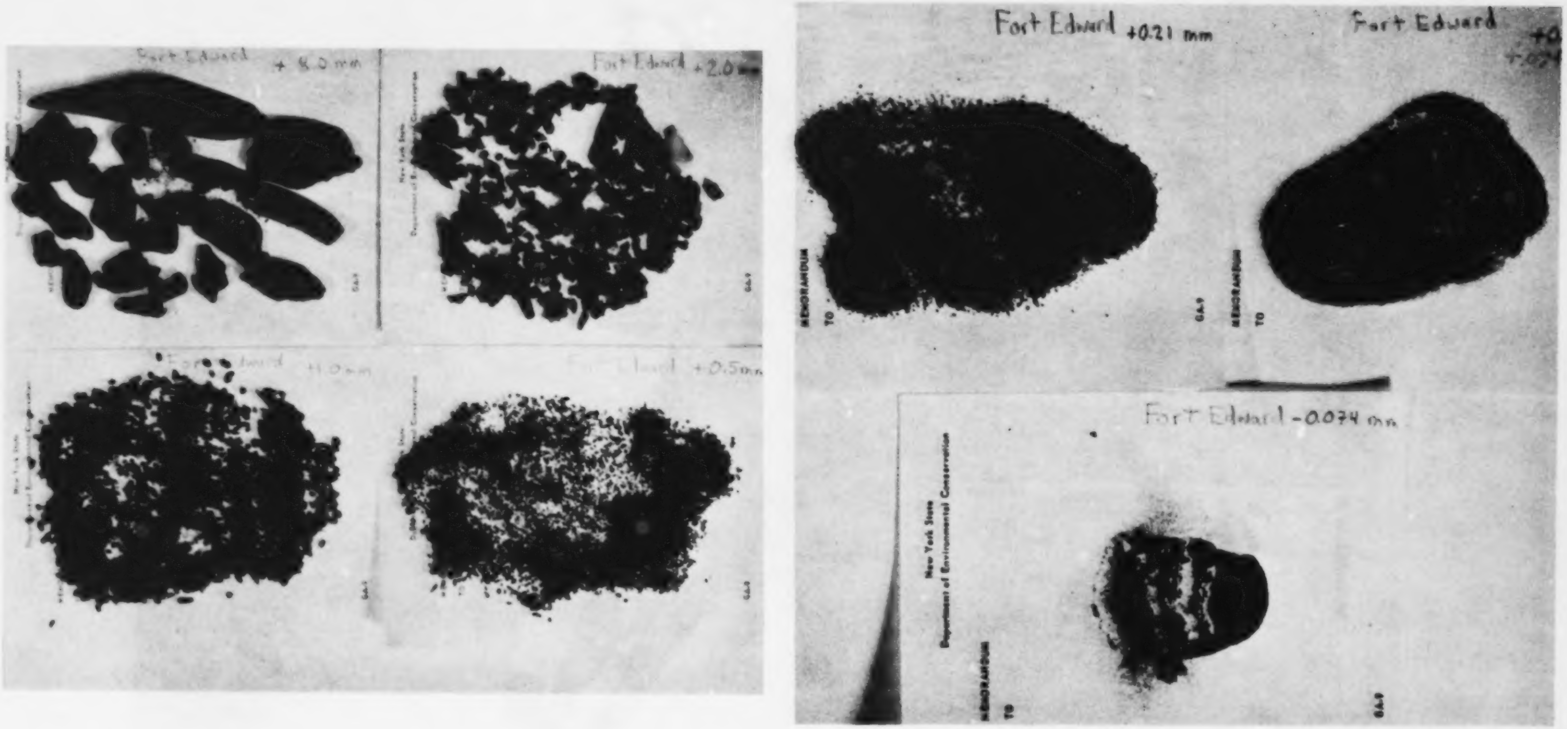
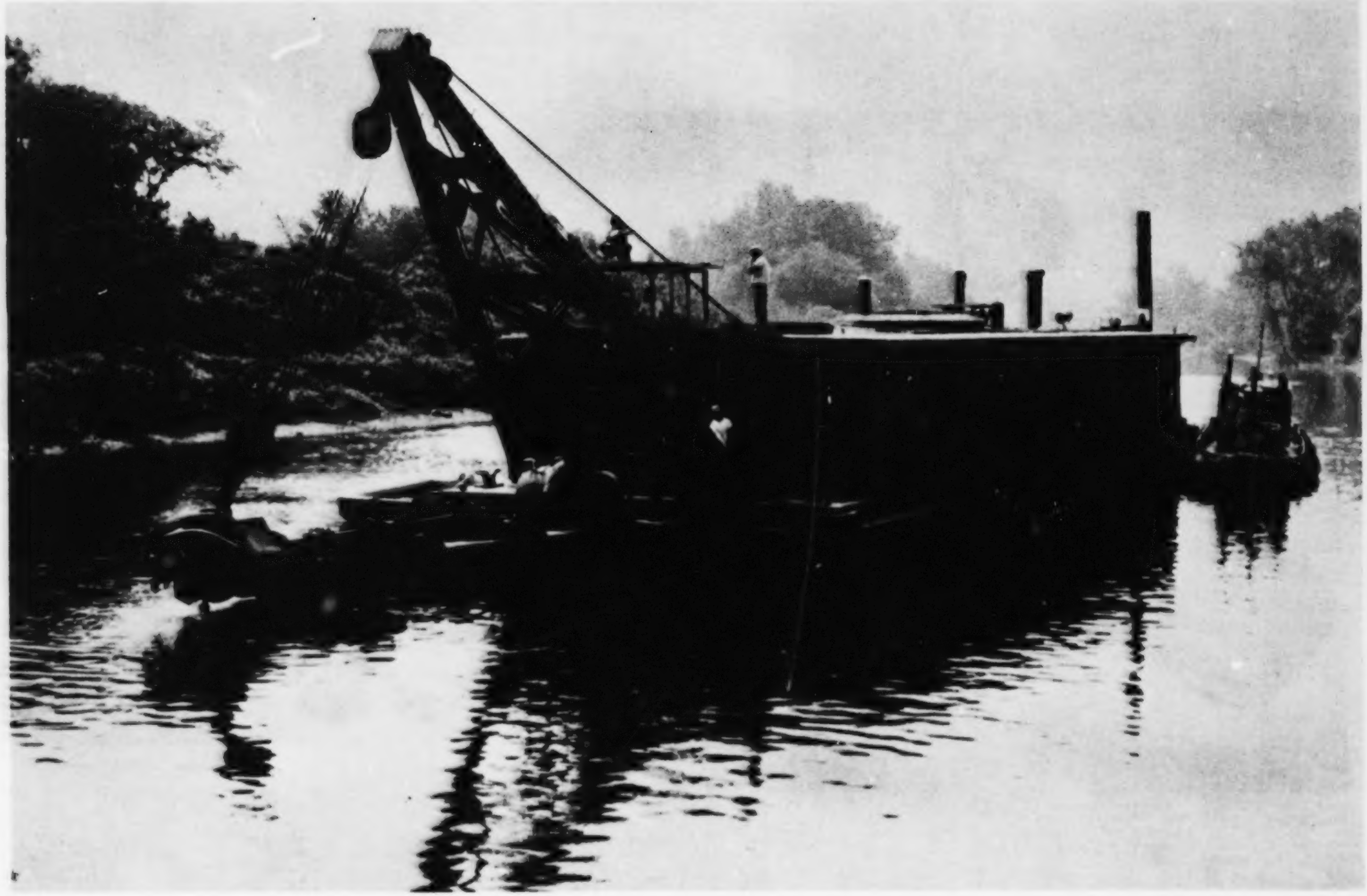

Fort Edward + 8.0 mm
Fort Edward +2.0 mm
Fort Edward +1.0 mm
Fort Edward +0.5 mm
Fort Edward +0.21 mm
Fort Edward +0.074
Fort Edward -0.074 mm
MEMORANDUM
TO
New York State
Department of Environmental Conservation

Figure 3
New York State Dept. of Transportation
Hydraulic Cutterhead Dredge



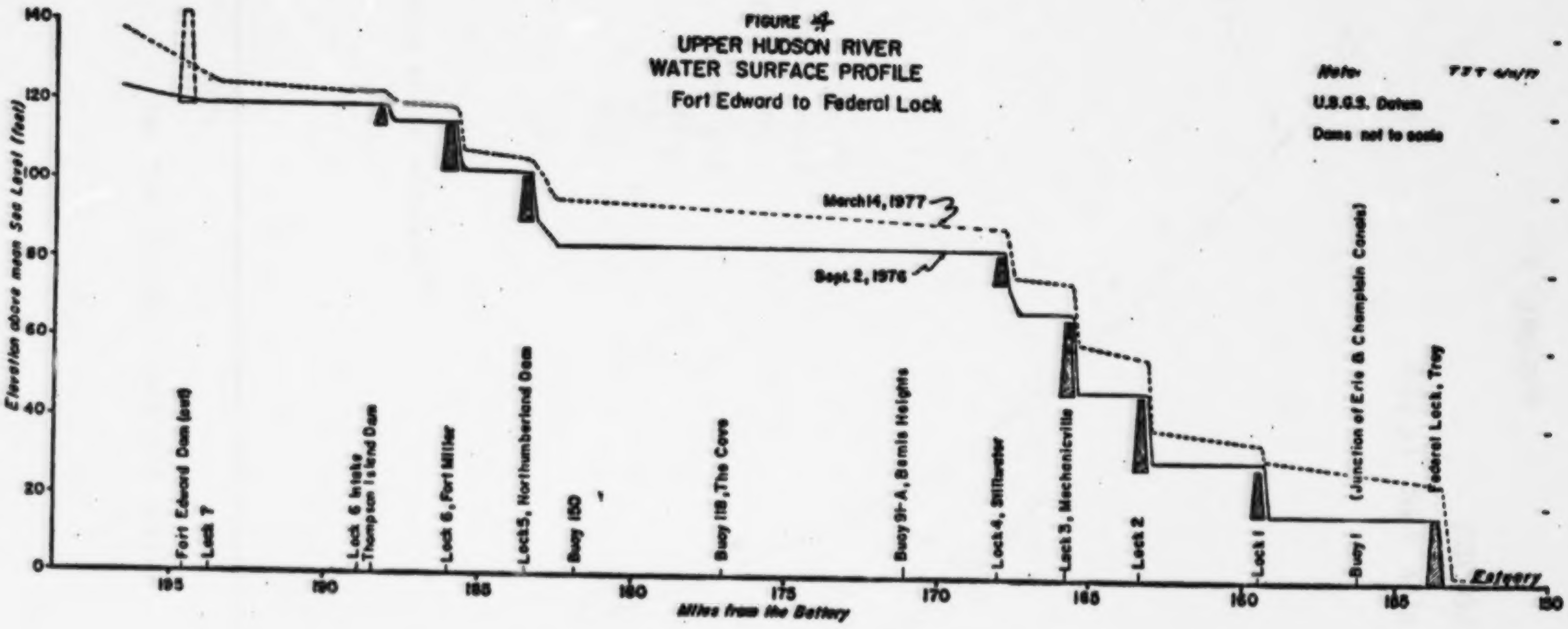


FIGURE 4

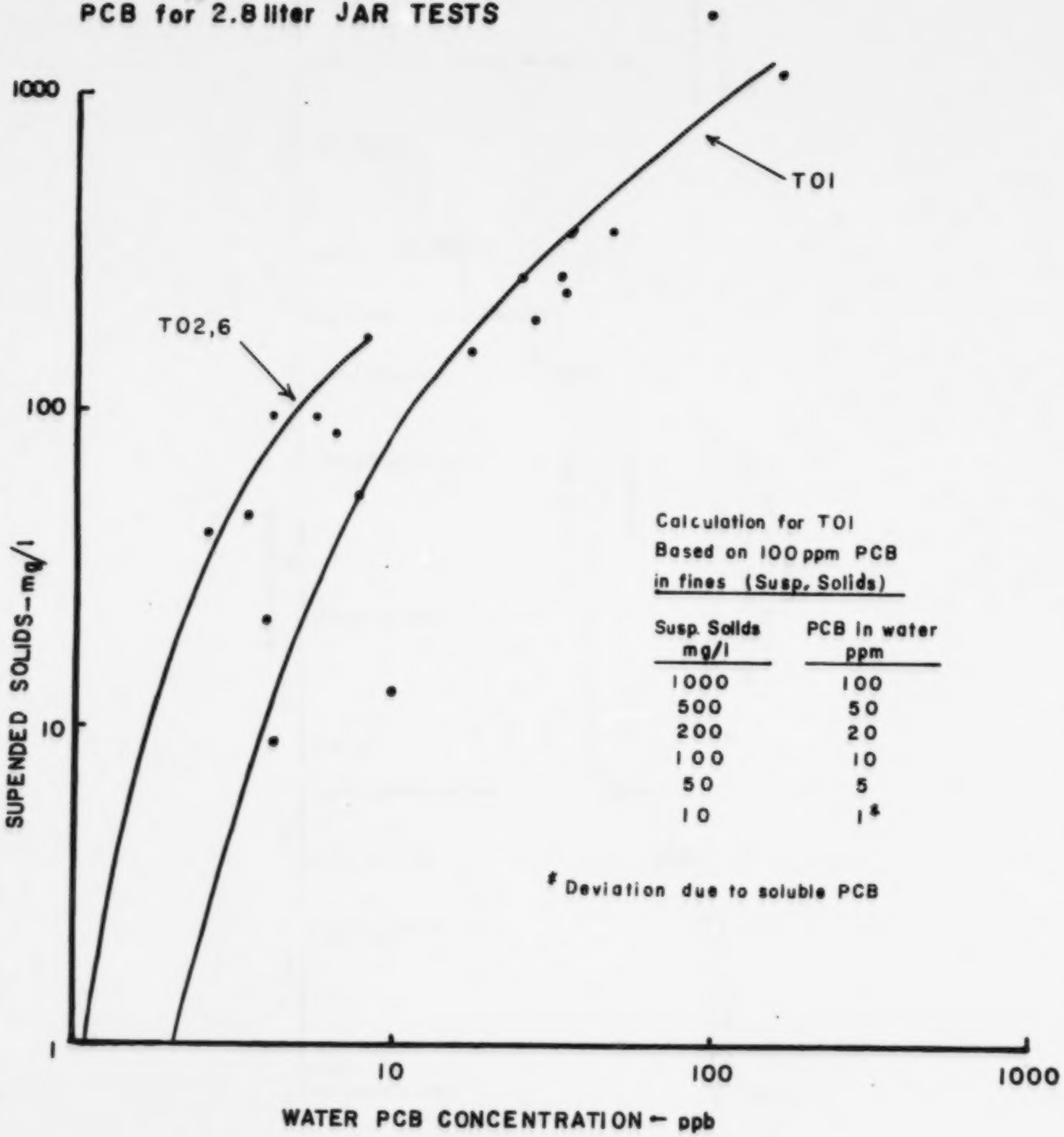
UPPER HUDSON RIVER
WATER SURFACE PROFILE
Fort Edward to Federal Lock

Note:
U.S.G.S. Datum
Dams not to scale

TJT 4/11/77

FIGURE 5

SUSPENDED SOLIDS
vs
PCB for 2.8 liter JAR TESTS

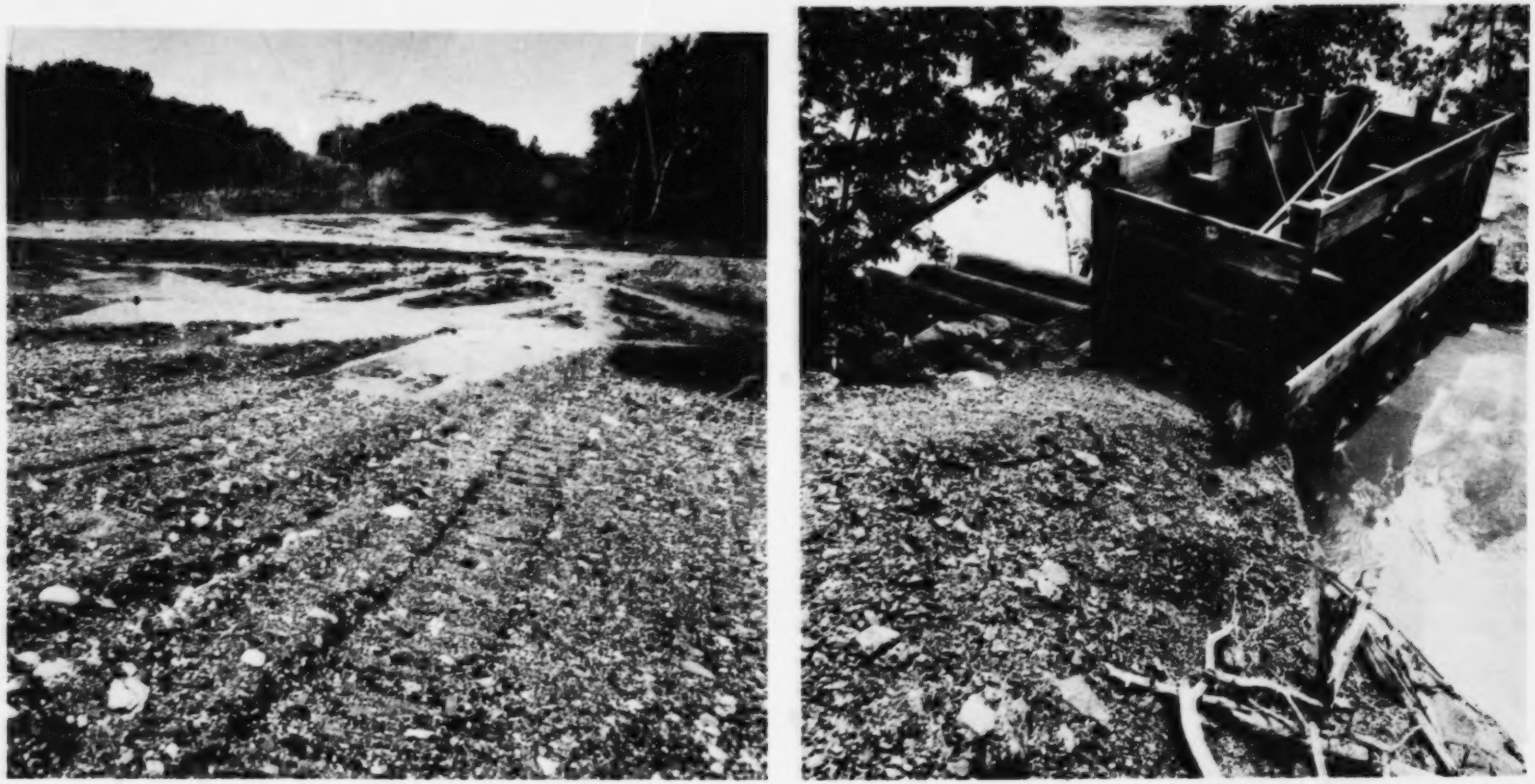


Calculation for T01
Based on 100 ppm PCB
in fines (Susp. Solids)

Susp. Solids mg/l	PCB in water ppm
1000	100
500	50
200	20
100	10
50	5
10	1*

* Deviation due to soluble PCB

Figure 6 - Lock 1 Dredging Spils Lagoon, June 1976



(Influent End)

(Effluent Box End)

Figure 7
Bouy 212 Dredging Spoils Lagoon
Showing Wood Chips and Sediment after Dewatering
October 1976

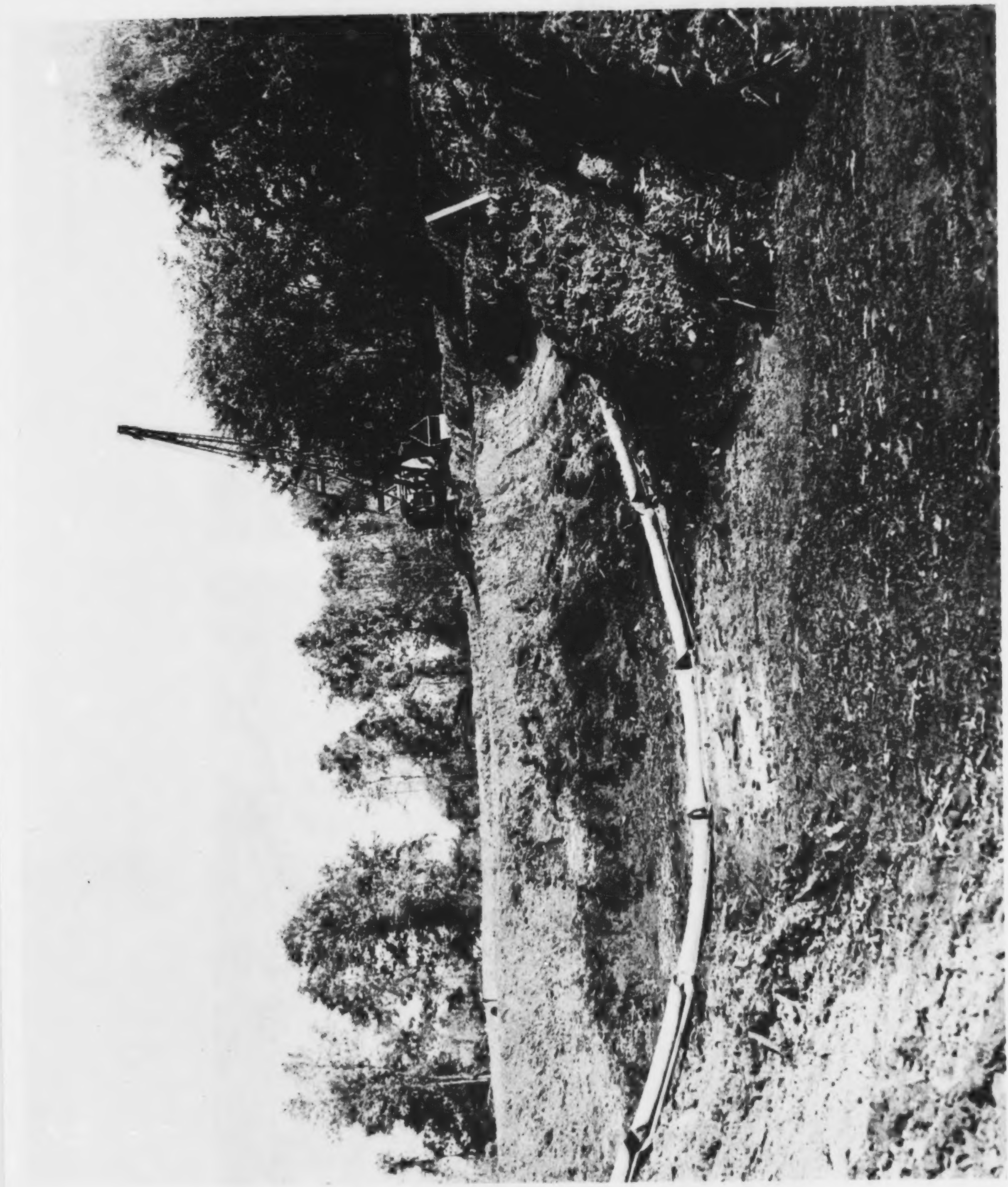


Figure 8
Bouy 212 Dredging Spoils Lagoon
Showing Scum Retention During Operation
October 1976

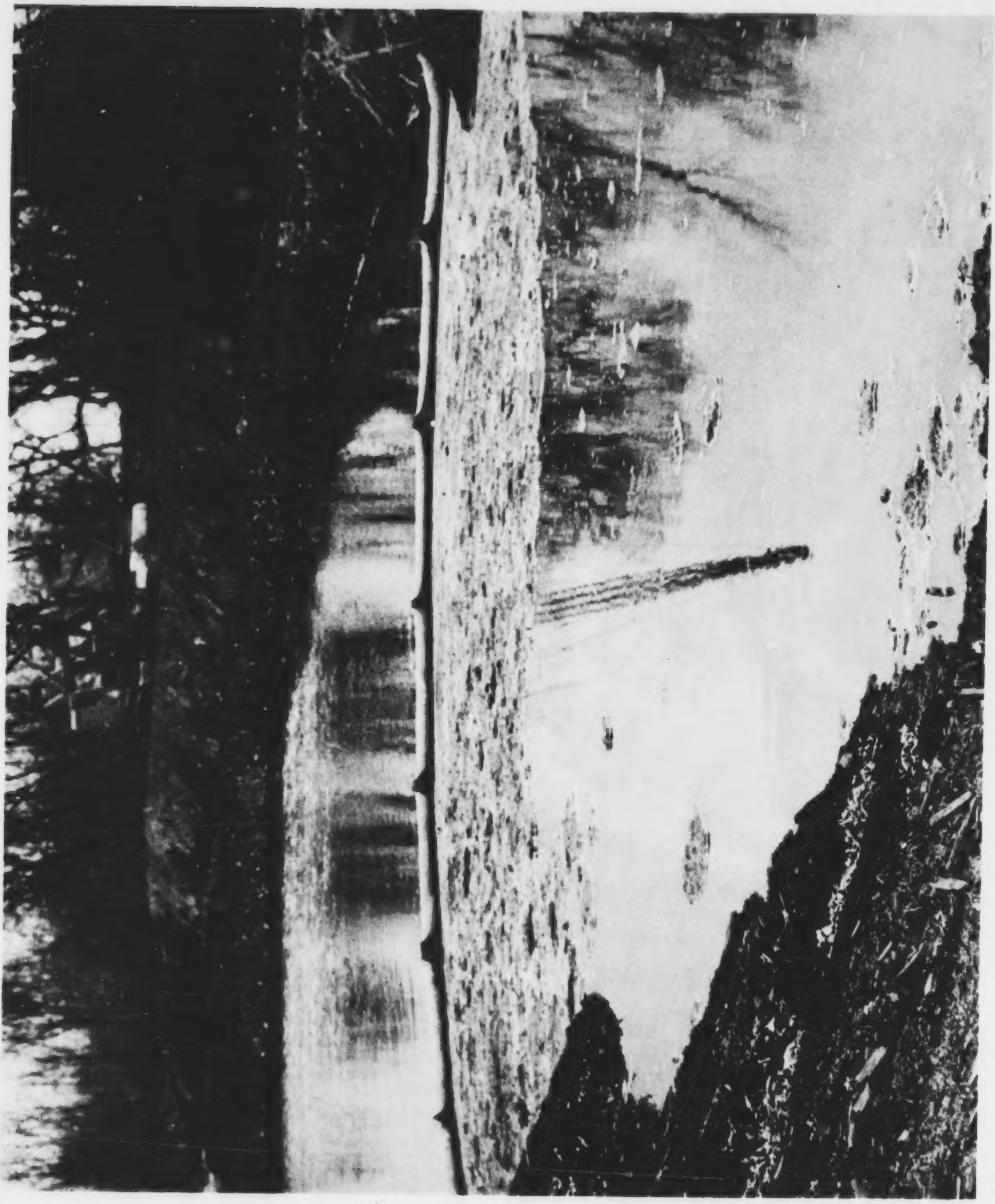


Figure 9 - Aerial Photograph of Lock 4
Dredging Spoils Site
September, 1977

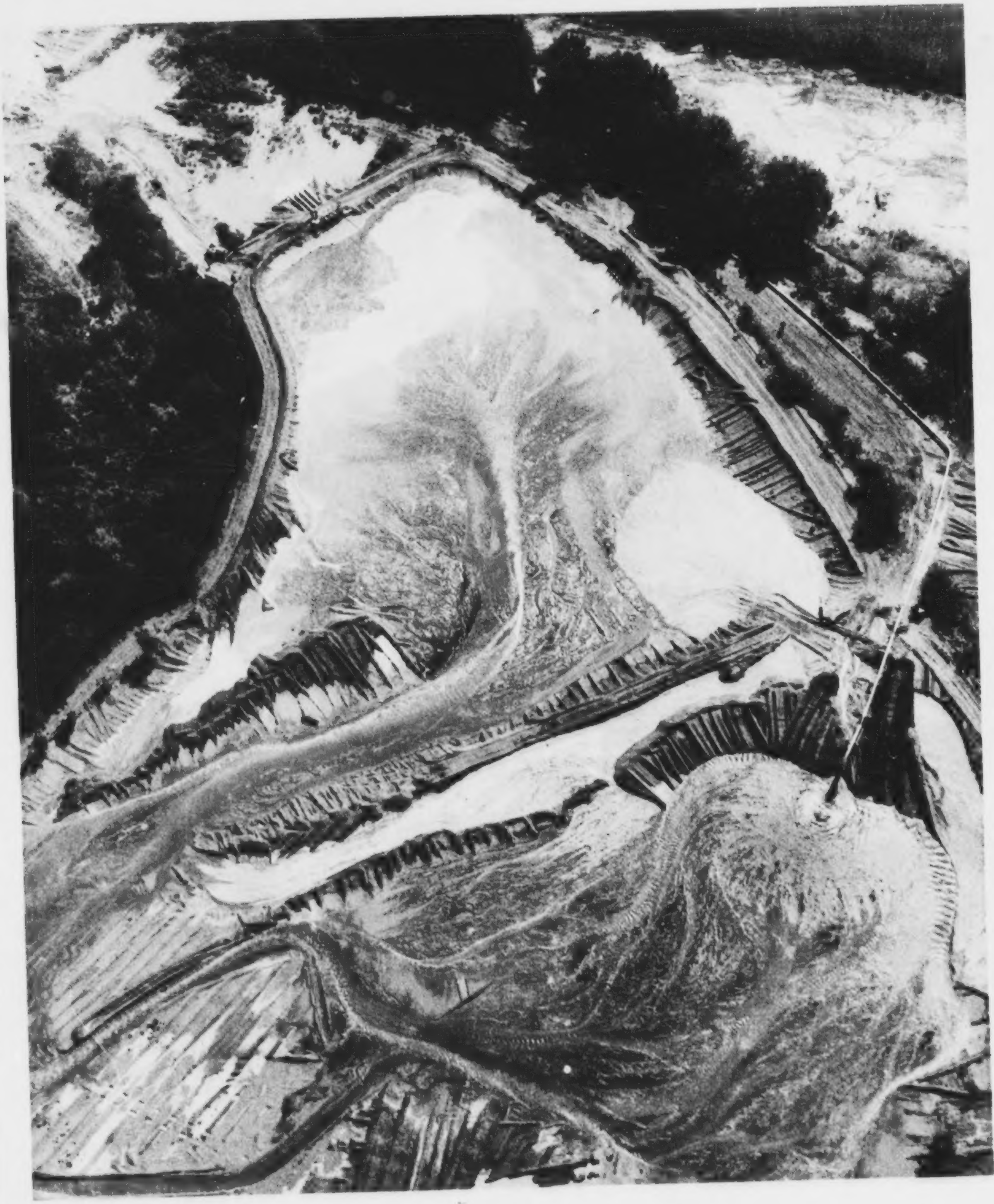
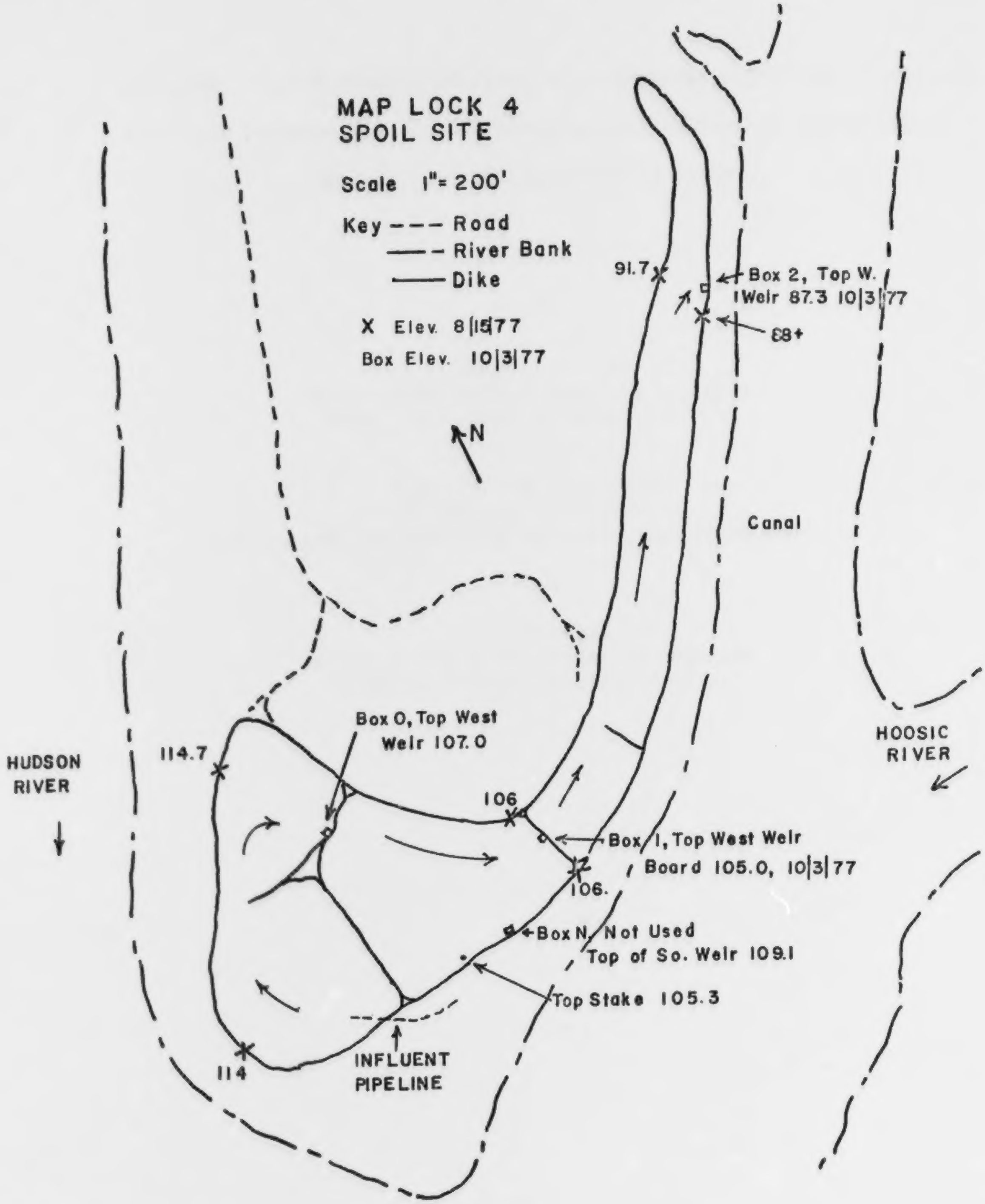


Figure 10


MAP LOCK 4
SPOIL SITE
Scale 1" = 200'
Key --- Road
—-- River Bank
—— Dike
X Elev. 8|15|77
Box Elev. 10|3|77
N
91.7
Box 2, Top W. Weir 87.3 10|3|77
88+
Canal
HOOSIC RIVER
HUDSON RIVER
114.7
Box 0, Top West Weir 107.0
106
Box 1, Top West Weir Board 105.0, 10|3|77
106.
Box N, Not Used Top of So. Weir 109.1
Top Stake 105.3
114
INFLUENT PIPELINE

The use of artificial substrates for monitoring toxic organic compounds: A preliminary evaluation involving the PCB (polychlorinated biphenyl) problem in the Hudson River, New York

by

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Introduction

The following report concerns our ongoing efforts to use multiplate sampling of macroinvertebrates for monitoring PCB (polychlorinated biphenyl) contamination in the surface waters of New York State. This method shows great promise for providing information not available from more conventional data, and it may be applicable to studies of other environmental contaminants.

Historical Development and Rationale

The severity of PCB contamination in the Hudson River has been well established through fish and sediment data (Spagnoli and Skinner, 1975; Nadeau and Davis, 1976; New York State Department of Environmental Conservation, 1976; U.S. Environmental Protection Agency, 1977). While these data are of obvious value in establishing the occurrence of PCB's in the river and its biota, they leave some important questions unanswered. The sediment data cannot predict the amount of contamination entering the food web or show the period(s) over which the PCB's accumulated. Because fish are highly mobile and fairly long-lived, it is difficult to know where and over what periods they assimilated these toxins.

Use of macroinvertebrates as indicators does not entail such limitations. Macroinvertebrates are part of the food web; and because they are relatively immobile and have short life cycles, any PCB's they contain will have been accumulated at a specific location and over a relatively short time.

Functionally, macroinvertebrates serve as an intermediate step in the food web, obtaining nutriment from detritus, various plants, and small animals and passing it on to larger animals, such as fish and waterfowl. In much the same way, they accumulate and transfer contaminants (such as chlorinated hydrocarbons) and are integral to the well-known process of biomagnification.

Sanders and Chandler (1972) have shown that aquatic invertebrates rapidly accumulate PCB's to levels several thousand times that of the surrounding water. When four species of aquatic insects were placed in water containing 1.1 to 2.8 parts per billion of Aroclor 1254, they accumulated between 5 and 30 parts per million in their body tissues after only 4 days, representing magnification factors of from 1,400 to 22,000. In a separate study, other immature insects (mayflies) accumulated PCB's by a factor of 1,950 after the same exposure period (Södergren and Svenson, 1973). This demonstrated ability to rapidly concentrate PCB's makes aquatic invertebrates valuable for monitoring surface water contamination. Since aquatic invertebrates are the mainstay in the diet of many fish, this approach will also monitor the approximate levels of contamination in fish food. This is particularly significant because food seems to be the main source of organochlorines (including PCB's) to fish (Addison, 1976).

Artificial substrate samplers have become popular in biological monitoring because they are relatively easy to use in most aquatic habitats and because they standardize several important sampling variables, including surface area and substrate type (Beak et al., 1973; Weber, 1973). They are of additional value in monitoring toxic substances, since they can obtain samples from the water column, for which data are often lacking. Samples collected in this manner not only can concentrate steady low levels, which are generally not detectable in grab water samples; they also will integrate intermittently high levels that would otherwise require continuous chemical monitoring.

Brief Description of Study Area

The investigation reported here was carried out in the main stem of the Hudson River from the village of Hudson Falls (mileage point 195) to Staatsburg (m.p. 85). In the short (4 miles) reach from Hudson Falls to Fort Edward the river is largely unregulated, generally flowing through a series on nonturbulent pools and shallow riffle areas. Moderate to heavy amounts of organic pollution (mainly treated sewage and paper mill wastes) enter the river at numerous intervals from Glens Falls to Fort Edward. Until May 1977 two major point sources of PCB's also entered the river in this reach.

From Fort Edward (m.p. 191) to Troy (m.p. 153) the river is used as part of the Champlain Canal and basically consists of a series of steplike navigation pools. Eight dams are used to regulate the height of the pools, and the main channel is dredged periodically to maintain the minimum width and depth requirements for navigation.

From Troy south (the Lower Hudson) the river is unregulated and is a true estuary: the river bed is below sea level, and a tidal rise and fall of about 4 feet is observed at the Troy dam. From Troy to Poughkeepsie (m.p. 70) the water is mainly fresh (limnetic zone). The oligohaline zone extends from Poughkeepsie to Haverstraw Bay (m.p. 30), where salinity generally ranges between 50 and 200 mg/l of Cl^-. From that point to the mouth salinity varies from 200 to 2000 mg/l of Cl^-, and the river is termed mesohaline (Howells, 1972).

Methods

A pilot project was undertaken in 1976 to determine the feasibility of using multiple (a type of artifical substrate) samplers to monitor PCB's in the water column of the Hudson River. The initial sampling network (Table I) consisted of 13 stations at 3-20-mile intervals between Hudson Falls and Staatsburg. Stations 1 and 3 were controls, located upstream from the known point discharges of PCB's in the Hudson River and Champlain Canal, respectively. The remaining stations were all below the discharges. Station 2 was in the "natural" river; stations 4-8, in the canalized Upper Hudson; and stations 9-13, in the limnetic zone of the Lower Hudson.

Because the results from 1976 were promising, the project was continued in 1977. Stations 14-16 were added, extending the sampling network into Haverstraw Bay, and station 3 (Champlain Canal) was dropped.

Samples were obtained by exposing hardboard artificial substrates for periods of 4-5 weeks. In 1976, they were installed in mid-May (12-17) and harvested approximately 4 weeks later (June 6-10). Subsequent collections were made at 5-week intervals (July 13-17; August 17-20; September 21-23). During 1977, samplers were installed on June 6-9 and Harvested July 11-14, August 15-18, and September 19-22. At the time of this writing, only the results from the August survey were available.

The actual sampling device was modified slightly from that originally described by Hester and Dendy (1962). Each sampler consisted of 10 plates of tempered hardboard (smooth on both sides), 6-inches (15.2-cm) square and 1/8-inch (0.3-cm) thick, mounted on a stainless steel turnbuckle. Plates 1-5 (counting from the top) were separated by hardboard spacers 1-inch (2.5-cm) square and 1/8-inch (0.3 cm) thick; plates 5-10, by spacers 1-inch square and 1/4-inch (0.6-cm) thick.

Two samplers were installed at each station. At stations 1-3 each sampler was suspended 3 feet (0.9 m) below the water surface from a half-gallon polyethylene float filled with Styrofoam packing material. A 4" x 8" x 16" cement block rested on the bottom and served as the anchor. At the remaining stations the samplers were suspended from navigation buoys at the same depth; a brick attached to the bottom of each unit provided some stabilization against the current. All connections were made with 1/8-inch plastic-coated cable, secured with cable clamps. Brass swivel snaps were used between the cable and sampler to facilitate removal and replacement of the samplers.

Several precautions were taken to reduce the contamination of the samples during harvesting. In particular, contact of the samples with paints and plastics was avoided, since these materials often contain PCB's (Bonner, 1976;

Peakall, 1975). In the laboratory all processing materials, including 14-quart galvanized steel buckets, wide-blade steel spatulas, and 1-quart glass jars, were washed with acetone, then rinsed with distilled water. A square of aluminum foil was placed over each jar before capping in order to prevent contamination from the paint and/or rubber gaskets on the jar lids. In the field, the exposed sampler was placed in a bucket, disassembled, and thoroughly cleaned by scraping off each plate with a wide-blade spatula. The slurry was then poured in a sample jar, which was placed on ice and returned to the laboratory for analysis.

In the laboratory, a portion of each sample was retained for identification of the organisms, and the remainder was submitted for chemical analysis. Originally we had intended to pick the organisms from the residue and have them analyzed separately. However, the fauna of the Hudson (especially near Fort Edward) is impaired by numerous industrial and municipal wastes and consists mainly of chironomid midges and oligochaete worms (Simpson, 1976). These organisms are so small that 10,000 to 15,000 individuals would be required to provide sufficient biomass for chemical analysis. To expedite the evaluation of this technique, the total residue from the samplers was analyzed. Less stressed rivers support a more diverse fauna, including relatively large organisms such as mayfly nymphs (Ephemeroptera) and caddisfly larvae (Trichoptera). Under those conditions, obtaining sufficient biomass for analysis would be much less of a problem.

To prepare the samples for chemical analysis, they were first filtered under suction on No. 41 Whatman filter paper. The retained solids were transferred to a soxhlet extraction thimble and extracted with acetone/hexane, 2:1 for 2 hours, then 1:1 overnight (16 hours). The residual material was dried at 70°C for 2 days and weighed to determine the dry weight of the sample. The two extracts were combined in a separatory funnel, and the lower aqueous phase was drawn off and reextracted with hexane in another separatory funnel. The combined hexane layers were dried over sodium sulfate and divided into two equal portions. One portion was evaporated to dryness (70°C for 2 days) and weighed to give the hexane-extractable fat content (this step was initiated in September 1976). The remainder was concentrated to 2 ml in a Kuderna-Danish evaporator, cleaned up by passage down a calibrated column of 2% deactivated Florisil (10 g; 1-cm diameter), overlaid with anhydrous sodium sulfate. A 40-ml fraction eluted with hexane was collected, evaporated to 1.5 ml, and analyzed with a Hewlett-Packard 5840A gas chromatograph with a ^{63}Ni detector. The column consisted of 1% Apiezon L (purified by eluting it from activated alumina with hexane and collecting the colorless fraction) on 110-120-mesh Gaschrome Q.

The quantity of PCB's in the sample was determined by measuring the areas of the peaks observed and dividing them by the peak areas of standard mixtures of Aroclor 1016 and 1242. The means of these results were used to calculate the quantity of PCB's per dry weight of material (Bush et al., 1975).

Results and Discussion

One of the prime concerns at the outset of this study was possible contamination of the samples from the sampling apparatus, particularly from the hardboard plates. Results from the two control stations ranged from 0.1 to 1.0 ppm (Table I) and indicated that contamination from the sampling method was minimal. Some PCB's were expected, since some contamination of the river sediments has been found in the area above the point discharges (N.Y. State Department of Environmental Conservation, 1976). To eliminate any possibility of contaminated hardboard, chemically inert porcelain plates could be used in constructing the multiplate samplers.

The results generated to date are providing an insight into the spatial and temporal distribution patterns of PCB's in the water column of the Hudson. During all sampling periods for which data are available, consistently higher concentrations have been found in the canalized portion of the Upper Hudson than elsewhere in the river (Table II). This is not surprising, since it is in this reach that the highest levels have been found in fish and sediments. Although PCB's are no longer being discharged by the General Electric facilities, substantial amounts are probably finding their way into the water from highly contaminated sediments. Concentrations as high as 3,707 ppm have been found in sediments accumulated behind the dams of the Upper Hudson (N.Y. State Department of Environmental Conservation, 1976).

Contamination of the Lower Hudson River, while less severe, was well above background levels. In June, July, and August 1976 all stations yielded PCB's in excess of 6 times background levels (Table II). The 100-year flood, which occurred in the spring of 1976, may have significantly increased the passage of PCB's from the upper to the lower river by resuspending and transporting PCB-laden sediments downstream. The Lower Hudson also receives contamination from a variety of other sources, such as the Mohawk River, various municipal and industrial outlets, and runoff (particularly leachates from landfills).

To this point we have considered the results expressed in parts per million per unit dry weight of the residue. Clayton et al. (1977) have shown, however, that lipid content is highly correlated with the PCB levels in marine invertebrates, and they contend that lipid content is the most meaningful normalization parameter for quantification of PCB results. Beginning in September 1976 we determined lipid content of the samples and thus have been able to normalize the results (Table III, Fig. 1)

The normalized data lead to the same general conclusion as the nonnormalized results, namely, that the greatest contamination is occurring in the canalized portion of the Upper Hudson. However, the two normalized profiles (Fig. 1) show a much more consistent pattern than the same data expressed per unit dry weight (Fig. 2). In both normalized curves, PCB concentrations progressively increase from the control station to Schuylerville, decrease slightly at Stillwater, then peak at Waterford and gradually diminish downstream. The disparity of the nonnormalized data is apparent in the reach from Fort Edward to Stillwater. In one profile there is a progressive decrease to Stillwater; in the other, a steady increase. The consistency of the normalized data confirm that this is a more reliable method of expressing the results.

The normalized data also show an interesting temporal change. The August 1977 profile is smoother, with Upper Hudson levels lower and Lower Hudson levels higher than in 1976. This suggests that PCB's are becoming more widely and evenly distributed throughout the river, although we do not know how much of this is attributable to the intervening 100-year flood. The hypothesis of a steady trend in this redistribution will be tested and reevaluated with data from additional surveys.

The results presented above are providing valuable information supplemental to fish and sediment data in the total assessment of PCB contamination in the Hudson River. Collection of aquatic invertebrates with artificial substrates will be continued to help evaluate the spatial and temporal distribution of PCB's throughout the river.

Summary and Conclusions

1. Multiplate samples are proving to be an effective means of monitoring PCB contamination in the water column of the Hudson River.

2. Results normalized to lipid content are more consistent than those

expressed per unit dry weight of residue.

3. Even with the abatement of the main point discharges in Fort Edward, PCB contamination is a continuing problem in Hudson River water. Concentrations are highest in the canalized Upper Hudson but seem to be becoming more evenly distributed throughout the river with the passage of time.

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Table I. Total PCB content of Multiplate Samples from Hudson River, New York (expressed as ppm PCB/dry weight of total residue).

Station	Location	Miles from mouth	June 1976	July 1976	Aug 1976	Sept 1976	Aug 1977
*1	Hudson Falls, near Chase Bag Co.	197	0.4	0.6	0.5	1.0	0.1
2	Ft. Edward, near Rt. 197 bridge	195	6.2	7.4	3.3	2.2	2.6
*3	Champlain Canal Ft. Edward	195	-	0.3	0.2	0.2	-
4	Ft. Edward, buoy 219	194	25.4	57.0	-	9.2	2.8
5	Ft. Miller, buoy 189	189	25.5	18.3	-	18.8	4.1
6	Schuylerville, buoy 147	182	12.5	12.4	-	11.8	8.9
7	Stillwater, buoy 81	169	23.8	-	-	9.0	10.8
8	Waterford, buoy 13	158	5.6	12.0	-	13.9	5.2
9	Troy, buoy 79	153	3.3	-	2.8	6.4	2.4
10	Castleton, buoy 53	136	4.9	10.5	200.0	11.0	2.8
11	Athens, buoy 88	116	2.6	5.0	9.0	0.0	3.4
12	Saugerties, buoy 39	102	3.2	11.0	4.5	1.0	-
13	Esopus, buoy 9	87	-	-	-	0.7	1.6
14	New Hamburg, Diamond Reef buoy	67	-	-	-	-	1.4
15	Peekskill, buoy 19	43	-	-	-	-	0.8

* Controls, upstream from the known point sources of PCB's.

Table II. Ranges of PCB concentrations for Upper and Lower Hudson Rivers compared with background levels (expressed as ppm PCB/dry weight of total residue).

Date	Background (stations 1 &/or 3)	Canalized Upper Hudson (stations 4-8)	Lower Hudson (stations 9-13)
June 1976	0.4	5.6-25.4	2.6- 4.9
July 1976	0.3-0.6	12.0-57.0	5.0-11.0
August 1976	0.2-0.5	no data	2.8-200.0
September 1976	0.2-1.0	9.0-18.8	0.0-11.0
*August 1977	0.1	2.8-10.8	0.8- 3.4

*Includes stations 14 and 15, added in 1977.

Table III. Multiplate PCB results normalized to lipid content (expressed as ppm PCB/mg lipids).

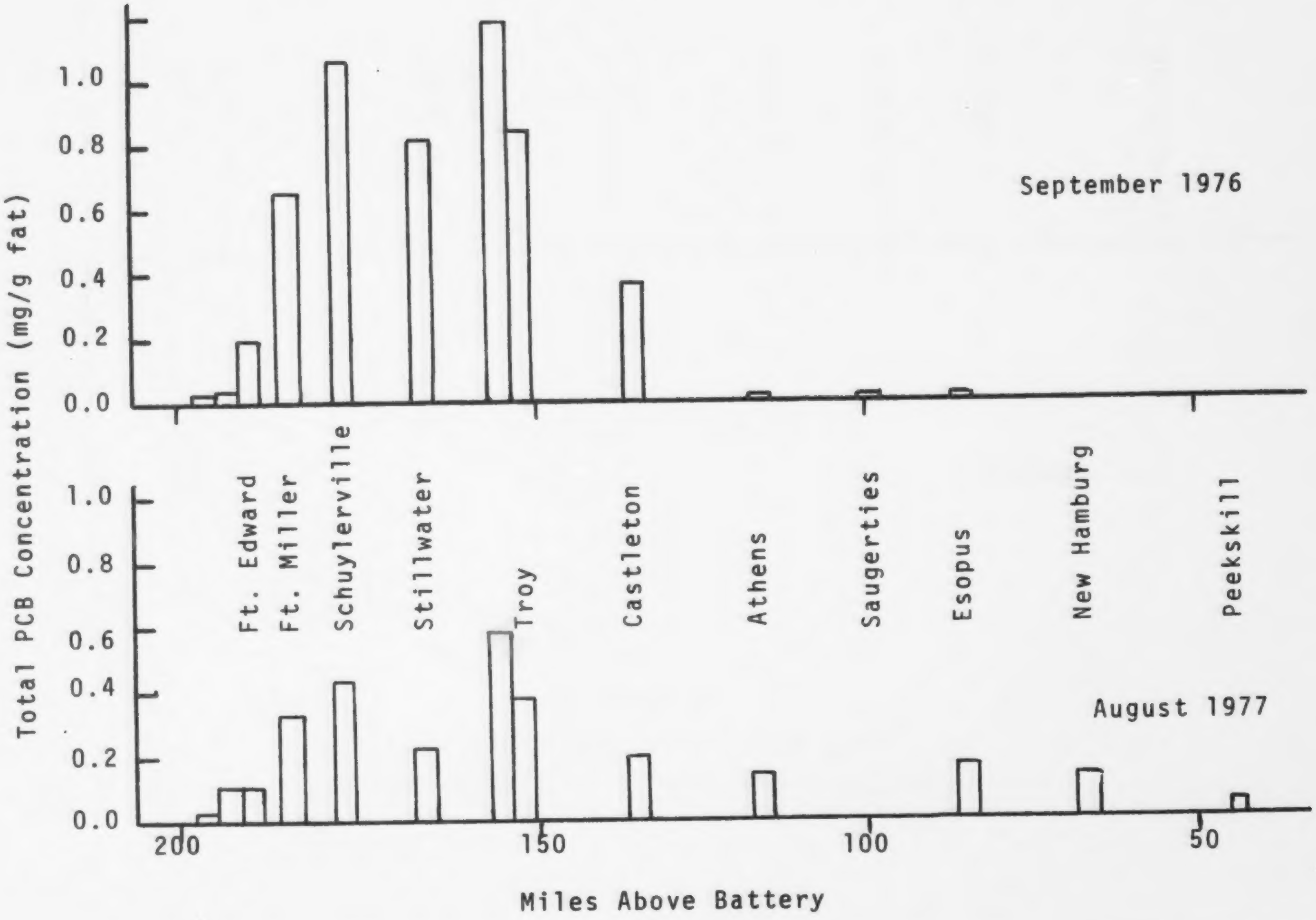
Station	Location	Miles from mouth	Sept. 1976	Aug. 1977
* 1	Hudson Falls, near Chase Bag Co.	197	0.055	0.005
2	Ft. Edward, near Rt. 197 bridge	195	0.088	0.100
*3	Champlain Canal Ft. Edward	195	-	-
4	Ft. Edward, buoy 219	194	0.186	0.095
5	Ft. Miller, buoy 189	189	0.640	0.323
6	Schuylerville, buoy 147	182	1.050	0.419
7	Stillwater, buoy 81	169	0.800	0.228
8	Waterford, buoy 13	158	1.150	0.589
9	Troy, buoy 79	153	0.820	0.383
10	Castleton, buoy 53	136	0.360	0.191
11	Athens, buoy 88	116	0.000	0.138
12	Saugerties, buoy 39	102	0.020	-
13	Esopus, buoy 9	87	0.010	0.176
14	New Hamburg, Diamond Reef buoy	67	-	0.133
15	Peekskill, buoy 19	43	-	0.058

* Controls, located upstream from the known point sources of PCB's.

HUDSON RIVER MULTIPLATE RESIDUES

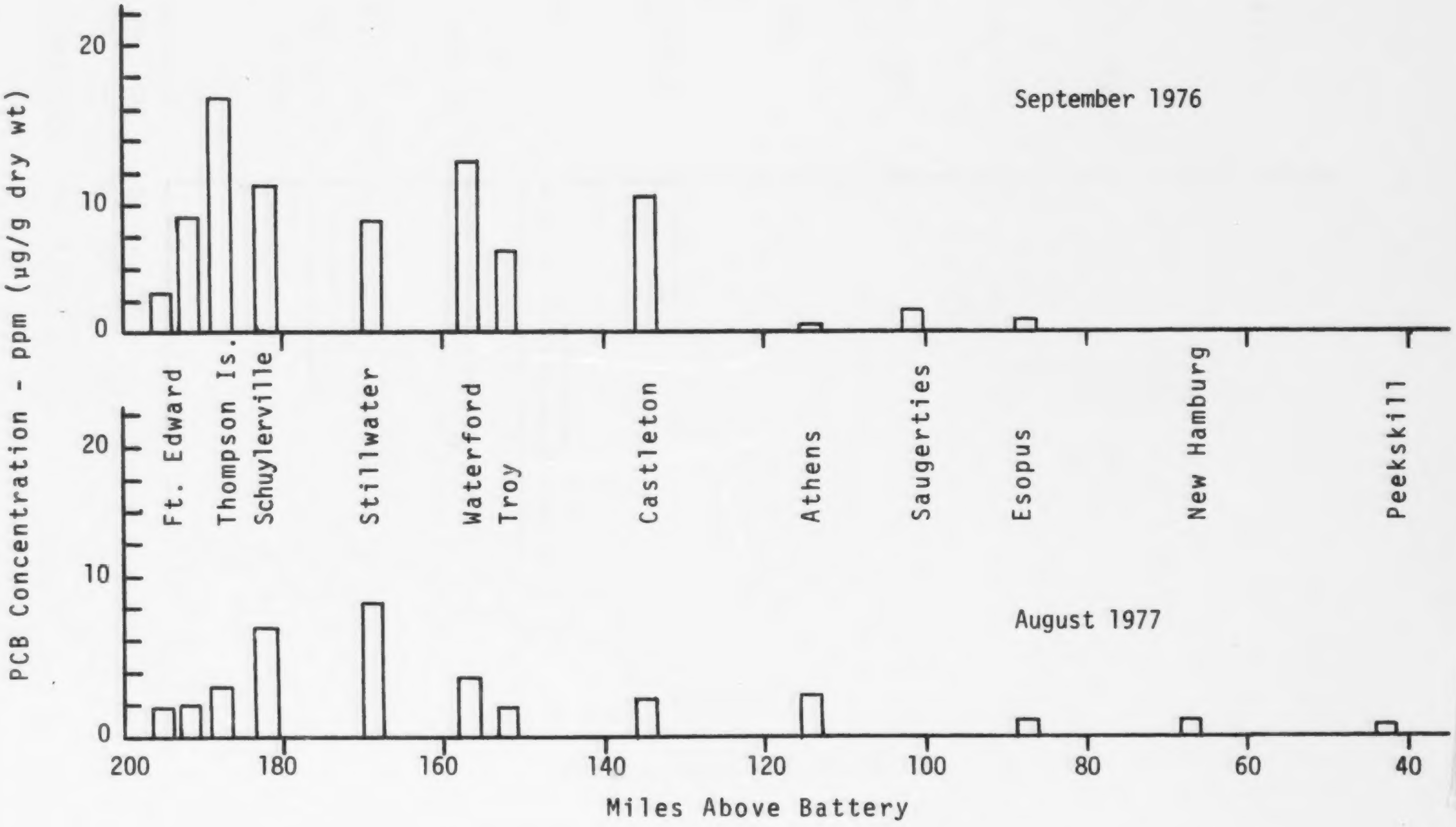
"NORMALIZED" PCB RESULTS

FIGURE 1



PCB CONCENTRATIONS IN MULTIPLATE RESIDUES FROM THE HUDSON RIVER, NEW YORK

Figure 2



RESEARCH PROGRESS ON REMOVAL OR TREATMENT OF PCB IN HUDSON RIVER SEDIMENT

BY: PM Griffen, AR Sears, CM McFarland

INTRODUCTION

An agreement signed with New York State in September 1976 stated that General Electric would conduct research and pilot plant studies on the removal or treatment of PCBs in sediments dredged from the Hudson River by the Department of Environmental Conservation. The agreement also stated that physical, chemical, and biological techniques should be considered.

Initial evaluations of the environmental situation revealed that PCBs have diffusely infiltrated into river sediments and large organic debris at the bottom of a high velocity region of the river. Due to this physical situation, in situ treatment approaches that require periodic additions, mechanical mixing, and subsequent reactant retrieval appear impractical. Consequently, GE investigators have concentrated on studies to minimize the quantity of material to be removed, maximize the effectiveness of controlled landfills, and demonstrate the usefulness of several separation, encapsulation, and destruction approaches.

Preliminary results have been encouraging. Rapid analytical procedures have been developed to reduce sample turnaround time from 24 hours to less than 2 hours thereby providing closer control over dredging operations. Indications of rapid PCB vaporization from spoil banks are being investigated, and the phenomena is being quantified under controlled laboratory conditions in appartus specifically designed for that purpose. Preparations have been completed for prototype investigations of distillation, excess air incineration, and limited air incineration on a 36 inch multiple hearth furnace with a high temperature after burner. Significant gains have been made in locating and culturing microbes which degrade the lower chlorinated biphenyls (less than 4 chlorines). To date, 15 different strains have been positively identified. They are currently being studied for nutrient, pH, and symbiotic requirements.

DISCUSSION

Aroclors 1016 and 1242 make up more than 85% of the PCBs found in Hudson River sediments below the General Electric Manufacturing facilities in Fort Edward down to the Troy dam. Concentrations of these Aroclors generally range from non-detectable to 100 parts per million(ppm) at depths of less than six inches. Deposits going as high as 1000 to 1500 ppm have been found but are contained in relatively small regions of the river. The cumulative effects of these sediment concentrations on aquatic life have not been resolved, nor has the movement of the PCB infiltrated sediments been scientifically predicted. (Both problems are currently under study by the NYS Department of Environmental Conservation). Consequently, the minimum allowable level permitted to remain in the river sediments has not been determined, the location of principal PCB deposits has not been established, and therefore, it has not been possible to calculate the total sediment volume to be removed. (Much of these data should be available by the end of 1977).

Pertinent characteristics of both the principal chlorinated biphenyls and the Hudson River bottom material are given in Tables I and II.

TABLE I

Specifications of Aroclor 1016/1242

Chlorine content	Approximately 42% by weight
Specific gravity	1.38 - 1.39 at 25°C
Distillation range	325 - 366°C
Evaporation loss (neat)	0 - 0.4% at 100°C for 6 hours
Decomposition temperature	600°C or less
Solubility in water	Less than 100 ppb
Solubility in organic solvents	Soluble

TABLE II

Specifications of Hudson River Sediments at Fort Edward

Organic content	10 to 30% by dry weight
Size distribution and composition	>6" organic rubble through fine clays
Maximum incineration temperature (clinker formation)	1200°C
PCB affinity *vs* size	Approximately equal amounts of PCB are found on all size fractions
Water content in settled solids	30 to 60%

Some information has been obtained regarding the problems of removing chemically infiltrated sediments and controlling their disposal. It was gained as a result of extensive dredging necessitated by the redeposition of large quantities of sediment from the region of the old Fort Edward dam (removed in 1973) to the Champlain shipping channel and the East channel at Fort Edward. About 800,000 cubic yards have been dredged to date by the Department of Transportation and placed in landfills along the river bank. In parallel, the NYS DEC availed itself of the opportunity to develop an approach for rapidly removing PCB from generated dredge waste water. Their approach, using flocculation and subsequent settling of suspended solids, reduced the total PCB concentration in the dredgate to a level of less than 50 parts per billion (ppb) prior to its return to the river. The concentration of PCB in the settled, dredged sediment appeared to average less than 30 ppm and has not presented a major leaching problem even from landfills with minimum control.

With these data and observations for background, NYS DEC has developed a program which addresses the following:

1. Determination of toxicity, amount, and location of PCB in river.
2. Postulation of significant ecological effects due to existing PCBs in the river and those which could be generated due to their removal for land storage.
3. Development of dredging techniques for the selective removal of material.
4. Generation of a model regarding PCB dissipation pathways from landfills so that storage facilities can be properly designed.
5. Selection and implementation of separation or destruction techniques if landfills cannot be properly constructed or maintained for safe and economical disposal of PCB infiltrated sediments.

General Electric's research program is aimed basically at Task 5 with areas of study selected from the list shown in Table III.

TABLE III

Possible Methods of Functional Treatment or Removal of PCB from Sediments

Approach	Techniques
Controlled storage	-Lagoons, pits, tanks, etc.
Fixation or Encapsulation	-Portland cement or polymer binder on dewatered sediments
Separation*	-Selective transfer and subsequent absorption direct from sediments to an activated carbon scavenger
	Filtration, flocculation, and clarification of suspended solids from supernatant
	Distillation and solvent extraction from settled sediments
	Plant and animal uptake from settled sediments
Destruction	-Incineration under either excess or controlled air conditions
	Chemical decomposition
	Enhanced microbial biodegradation
	Photodegradation
Natural Dissipation	-Vaporization
	Leaching
	Physical transport
	Natural biodegradation

*Each of these approaches must be combined with storage or destructive techniques to accomplish an acceptable disposal.

A prime factor in the selection of a specific research approach was the necessity to couple with current river sediment extraction techniques. Since the technology of dredging today is based upon a long-term evolution of equipment designs for removing large quantities of sediments in the shortest possible time and lowest cost, selectivity or precision of removal has not been an important factor. Now, with attention being directed towards retrieval of specific materials from water bodies followed by the disposal of the extracted material, selectivity has acquired a much higher priority.

Without the ability to remove specific material, large quantities of "clean" sediment will be unnecessarily processed at an undue cost in time and money. The reasons for poor precision are many. They include inadequate mapping, sediment instability, and the inability of the dredge operator to detect the boundaries of the deposit.

General Electric has been able to have an impact on this situation by developing analytical techniques that will provide data on PCB concentrations in the sediments while the dredging operation is in progress.

Once the sediment has been determined to contain higher than acceptable levels of PCB, it can be transported to previously prepared controlled storage areas. Within these storage areas, the forces of nature will act to slowly degrade or dissipate PCBs through natural microbial action, soil chemistry, volatilization, leaching, photodegradation, and physical transport by erosion or terrestrial animals. Some of these pathways can be controlled by dredge site design. Those which are not properly understood are under investigation by DEC, subcontractors for DEC, and General Electric.

Decisions will be made in late 1977 or early 1978 as to what must be done to PCB infiltrated sediments contained in controlled landfills. If PCB removal or treatment is deemed necessary, by the State, the results of General Electric's investigations will be utilized.

PRELIMINARY CONCLUSIONS

PCBs have become diffusely distributed to the environment from point sources all over the world. Retrieval of these chemicals is technically feasible although extremely expensive. If future studies of ecological effects show evidence that outweighs the economic issue, then methodologies such as rapid detection, selective removal, controlled storage, incineration, and biodegradation will become highly developed and the every day tools of the environmental engineer.

SESSION IV

"Current Research on the Fate and Effect of Kepone"

CHAIRMAN

Dr. Tudor Davies
Deputy Director
Environmental Research Laboratory at Gulf Breeze
Office of Research and Development
U. S. EPA

SPEAKERS

Mr. David J. Hansen
Research Aquatic Biologist
Environmental Research Laboratory at Gulf Breeze
U. S. EPA
"Effects of Kepone on Estuarine Organisms"

Mr. Steven C. Schimmel
Research Aquatic Biologist
Environmental Research Laboratory at Gulf Breeze
U. S. EPA
"Acute Toxicity of Kepone to Four Estuarine Animals"

Mr. Lowell H. Bahner
Research Aquatic Biologist
Environmental Research Laboratory at Gulf Breeze
U. S. EPA
"Kepone Accumulation and Food Chain Transfer"

Richard L. Garnas, Ph.D.
Research Scientist
Environmental Research Laboratory at Gulf Breeze
U. S. EPA
"Fate and Degradation of Kepone in Estuarine Microcosms"

Robert J. Hugget, Ph.D.
Project Manager
The Virginia Institute of Marine Science
"The Role of Sediments in the Storage, Movement and Biological Uptake of Kepone in Estuarine Environments"

Donald J. O'Connor, Ph.D.
Environmental Engineering and Science Program
Manhattan College
"Preliminary Analysis of Kepone Distribution in the James River"

Effects of Kepone® on Estuarine Organisms[1]

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ABSTRACT

Laboratory toxicity tests were conducted to determine the effect of Kepone on and its accumulation by estuarine algae, mollusks, crustaceans, and fishes. Nominal Kepone concentrations calculated to decrease algal growth by 50 percent in static bioassays lasting seven days were: 350 μg/ℓ, Chlorococcum sp.; 580 μg/ℓ, Dunaliella tertiolecta; 600 μg/ℓ, Nitzschia sp.; and 600 μg/ℓ, Thalassiosira pseudonana. Measured Kepone concentrations calculated to cause 50 percent mortality in flowing-seawater toxicity tests lasting 96 hours were: 10 μg/ℓ for the mysid shrimp (Mysidopsis bahia); 120 μg/ℓ for the grass shrimp (Palaemonetes pugio); >210 μg/ℓ for the blue crab (Callinectes sapidus); 70 μg/ℓ for the sheepshead minnow (Cyprinodon variegatus); and 6.6 μg/ℓ for the spot (Leiostomus xanthurus). Bioconcentration factors (concentration in

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® Registered trademark, Allied Chemical Corporation, 40 Rector Street, New York, New York 10006. Kepone was purchased from Chem Service, West Chester, PA as 99% pure. Our analyses indicated 88% purity.

[1] Contribution No. 311, Environmental Research Laboratory, Gulf Breeze.

whole animals divided by concentration measured in water) in these tests were greatest for fishes (950 to 1,900) and less for grass shrimp 420 to 930.

Survival, growth, and reproduction of mysids and sheepshead minnows were decreased in chronic bioassays lasting 14 to 64 days. Growth of mysids and sheepshead minnows was reduced by exposure to 0.07 $\mu g/\ell$ and 0.08 $\mu g/\ell$ respectively. Bioconcentration factors for sheepshead minnows in the chronic bioassay averaged 5,200 (range 3,100 to 7,000) for adults exposed for 28 days and 7,200 (3,600 to 20,000) for juveniles exposed for 36 days. The chronic toxicity and bioconcentration potential of Kepone are more important factors than its acute toxicity in laboratory evaluations of environmental hazard. Therefore, these factors should be considered when attempting to assess present impacts and attempting to limit future impacts of this insecticide on the aquatic environment.

INTRODUCTION

Kepone (decachlorooctahydro-1,3,4-metheno-2H-cylobuta [cd] pentalene 2-one) is an insecticide that was manufactured and formulated in the United States to control ants, cockroaches and insect pests of potatoes and bananas. Kepone is toxic to birds and mammals including man (Jaeger, 1976) and acutely toxic to some estuarine organisms (Butler, 1963). Recent contamination of water, sediment, and biota in freshwater and estuarine portions of the James River, Virginia has stimulated concern about this chemical's hazard to aquatic biota (Hansen et al., 1976). This concern was based on (1) the continued occurrence of Kepone in many finfishes and shellfishes in amounts that forced closure of fishing because of potential human health hazard and (2) laboratory studies which showed that Kepone is highly bioaccumulative and toxic to estuarine organisms, particularly in chronic exposures. This paper describes the results of these laboratory toxicity tests with estuarine algae, oysters, crustaceans, and fishes and chronic tests with a crustacean and a fish.

Experimental Procedures

Acute Toxicity

Algae: The unicellular algae Chlorococcum sp., Dunaliella tertiolecta, Nitzschia sp., and Thalassiosira pseudonana were exposed to Kepone for seven days to determine its effect on growth (Walsh et al., In press). Algae were cultured in 25 or 50 ml of growth media and artificial seawater of 30 °/oo salinity and a temperature of 20°C (Hollister et al., 1975). Kepone, in 0.1 ml acetone, was added to culture media and 0.1 ml of acetone was added to control cultures. Photoperiod consisted of 12 hours dark and 12 hours of 5000 lux illumination. Effect on growth was determined by electrophotometrically measuring optical density. Also, algae grown for 6 days in media and then exposed to 100 μg/ℓ Kepone for 24 hours were analyzed for Kepone content.

Oysters: The acute toxicity of Kepone to embryos of the eastern oyster (Crassostrea virginica) was determined by measuring its effect on development of fully-shelled, straight-hinged veligers in a 48 hour static exposure[1]. Methods used were those of Woelke (1972) and U.S. EPA (1975). Test containers were 1-ℓ glass jars that contained 900 mℓ of 20°C, 20 °/oo salinity seawater and 25,000 ± 1,000 oyster embryos. All test concentrations were triplicated. The number of normal and abnormal embryos were counted microscopically in a Sedgewick-Rafter cell at the end of 48 hours of exposure to Kepone.

Crustaceans and Fishes: The acute toxicity of Kepone to grass shrimp (Palaemonetes pugio), blue crabs (Callinectes sapidus), sheepshead minnows (Cyprinodon variegatus), and spot (Leiostomus xanthurus) was determined in

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[1] This research was performed under an EPA contract by Mr. Tom Heitmuller, Bionomics-EG&G, Inc. Marine Research Laboratory, Pensacola, Florida 32507.

96-hour flow-through toxicity tests (Schimmel and Wilson, In press). Acclimation and testing procedures were compatible with those of Standard Methods (A.P.H.A., 1971). Test animals were caught locally and 20 were placed in each 18ℓ aquarium. Water flow to each aquarium was 68 ℓ/hour. Stock solutions of Kepone in acetone were metered into experimental aquaria at the rate of 60 mℓ/hour. Control aquaria received 60 mℓ of acetone/hour. At the end of the experiment, surviving animals were chemically analyzed for Kepone content.

The acute toxicity of Kepone to mysids (Mysidopsis bahia) was determined by using intermittent flows of water from a diluter (Mount and Brungs, 1967) or continuous flow of water from a siphon and Kepone from an infusion pump (Bahner et al., 1975). Thirty-two 48-hour-old juvenile mysids were placed in chambers (4 mysids per chamber), in each test aquarium. Chambers consisted of glass petri dishes to which a 15 cm. tall cylinder of 210μ mesh nylon screen was glued. Water in the chambers was renewed by a self-starting siphon which nearly emptied and then filled each aquarium at about 25 min. intervals.

Chronic Toxicity

Mysidopsis bahia: The chronic toxicity of Kepone to this mysid was determined in 19-day exposures that began with 48-hour-old juveniles. (Nimmo et al., In press). This permitted time for production of several broods for assessment of reproductive success and survival of progeny. Exposure conditions, apparatus, and number of mysids per concentration were identical to those of the acute toxicity tests. Three tests were conducted; one to assess effects on survival and reproduction and two, at lower concentrations, to determine effects on growth. Data from the two growth experiments were pooled for statistical analysis.

Cyprinodon variegatus: The chronic toxicity of Kepone to sheepshead minnows was determined in a 64-day flow-through bioassay; 28-day adult exposure followed by a 36-day exposure of their progeny (Hansen, et al., In press). We delivered Kepone, 0.0088 μℓ of the solvent triethylene glycol, and 1.5ℓ of filtered 30°C seawater (average salinity 15 °/oo; (range, 8-26 °/oo) to each 70ℓ aquarium during each of 440 daily cycles of the dosing apparatus of Schimmel et al. (1974). Seawater and solvent were delivered to the control aquarium. Thirty-two adult females and 32 adult males were exposed to each concentration of Kepone for 28 days. Egg production was enhanced using injections of 50 international units of human chorionic gonadotrophic hormone on exposure day 25 and 27 (Schimmel et al., 1974). Eggs were fertilized on day 28 and placed in chambers, glass petri dishes with 9-cm tall cylinders of 450μ nylon mesh. Twenty embryos were used in each chamber. Embryos from control fish were placed in four chambers in the control aquaria and in four chambers in each of the six aquaria receiving Kepone. Embryos from fish in each of the six aquaria receiving Kepone were placed in four chambers in that aquarium and in four chambers in the control aquarium. Water in the chambers was exchanged by the action of a self-starting siphon in each aquarium that caused water levels to fluctuate 5 cm about 40 times per day. In the 36-day exposure to determine Kepone's effect on survival and growth of progeny, embryos hatched, and fry grew until they were juvenile fish. Kepone content of adult fish, their eggs, and juvenile fish was determined.

Statistical Analyses

Probit analyses of growth and mortality data were used to determine EC50's and LC50's. Growth data for M. bahia were subjected to analysis of variance (α = 0.05) and for C. variegatus, analysis of covariance and Newman-Kuels tests (α = 0.01) was used.

Chemical Analyses

Water from acute and chronic tests with crustaceans and fishes, and organisms surviving these tests, were analyzed by gas chromatography. Methods of extraction concentration, cleanup, and quantification were described by Schimmel and Wilson (In press).

Results and Discussion

Acute Toxicity

Algae: Growth of marine unicellular algae was reduced by exposure to Kepone in static tests (Table 1). Chlorococcum was the most sensitive of the four algae tested with a 7-day EC50 of 350 μg/ℓ. The three less sensitive species responded similarly to Kepone with overlapping confidence limits for EC50's. Algae exposed to 100 μg Kepone/ℓ of media accumulated the chemical with Chlorococcum containing 0.80 μg/g; D. tertiolecta, 0.23 μg/g; Nitzschia, 0.41 μg/g; and T. pseudonana, 0.52 μg/g. Butler (1963) reported that when estuarine phytoplankton were exposed to 1,000 μg/ℓ carbon fixation was reduced by 95 percent.

Oysters: The 48-hr EC50 for oyster larvae in static tests was less than those of algae (Table 1). The EC50, calculated using nominal water concentrations, was 66 μg/ℓ[2]. Embryos from 56 μg/ℓ were fully shelled and straight-hinged but appeared smaller than those from controls. The percentage of normal embryos in 65 μg/ℓ was 32 percent and in 87 μg/ℓ it was 0 percent. The concentration of Kepone calculated to reduce shell deposition of juvenile eastern oysters by 50 percent in a 96-hour flowing water bioassay was 38 μg/ℓ in water of 14°C and 11 μg/ℓ in water of 31°C (Butler, 1963).

Crustaceans and Fishes: Kepone, at the concentrations tested, was acutely toxic to mysids (Nimmo et al., In press), grass shrimp, sheepshead minnows, and spot but not to blue crabs (Schimmel and Wilson, In press) (Table 1). Spot and mysids were the more sensitive species with 96-hour LC50 values of 6.6 and 10 μg/ℓ. Crabs exposed to as much as 210 μg Kepone/ℓ suffered no significant mortality. Symptoms of acute Kepone poisoning in fishes included lethargy, loss of equilibrium and darkened coloration on the posterior portion of the body; occasionally only in one quadrant. Crustaceans became lethargic before death but exhibited no color change. Butler (1963) reported forty-eight hour LC50 or EC50 values (based on nominal concentrations) for other estuarine organisms were: Brown shrimp (Penaeus aztecus) 85 μg/ℓ, longnose killifish (Fundulus similis) 84 μg/ℓ, and white mullet (Mugil curema) 55 μg/ℓ.

Kepone was bioconcentrated from water by all four species we exposed for 96 hours. Bioconcentration factors (concentration in tissue divided by measured Kepone in water) for fishes were similar (950 to 1,900). Bioconcentration factors for grass shrimp ranged from 420 to 930 and for blue crabs 6 to 10.

Chronic Toxicity

Mysidopsis bahia: Exposure of this mysid to Kepone for 19 days in the first experiment decreased its survival and reduced the number of young produced per female (Table 2) (Nimmo et al., In press). At the highest concentration (8.7 μg/ℓ) all mysids were dead within the first two days. At lesser concentrations (1.6 and 4.4 μg/ℓ) mortality continued throughout the test. Eighty-four percent of the mysids survived exposure to 0.39 μg Kepone/ℓ water and

91% survived in control aquaria. In addition, natural reproduction was affected. Average number of young mysids produced per female was 15 in control, 9 in 0.39 μg/ℓ, and none in 1.6 μg/ℓ. Mysids that survived throughout the Kepone exposure appeared smaller than those in control aquaria, therefore, two additional experiments were conducted to measure Kepone's effect on growth.

In these experiments, the average length (tip of carapace to end of uropod) of mysids exposed to Kepone was decreased (Nimmo et al., In press). Females exposed to 0.072, 0.11, 0.23, or 0.41 μg/ℓ were significantly shorter than were control mysids; average length was 8.2 mm for exposed versus 8.6 mm for control female mysids. Unexposed and exposed males, however, were of similar average lengths, 7.7 to 8.0 mm.

Cyprinodon variegatus: Kepone was toxic to adult sheepshead minnows exposed for 28 days (Table 3). Symptoms of poisoning included : scoliosis, darkening of the body posterior to the dorsal fin, hemorrhaging near the brain, edema, fin-rot, uncoordinated swimming and cessation of feeding. Symptoms were first observed on day one in 24 μg/ℓ, two in 7.8 μg/ℓ, three in 1.9 μg/ℓ, and day eleven in 0.8 μg/ℓ. Mortalities began 5 to 8 days after onset of symptoms.

Kepone affected the progeny of 28 day exposed adults. In Kepone-free water, mortality of embryos from adults exposed to 0.05 to 0.8 μg/ℓ was similar to that of embryos from unexposed adults (range 6 to 12 percent). However, in Kepone-free seawater, 25 percent of the embryos from fish exposed to 1.9 μg of Kepone/ℓ died; abnormal development of 13 of these 20 embryos preceded mortality.

Table 1. Acute toxicity of Kepone to estuarine organisms. Algal and mollusk toxicity tests were static and estimated nominal concentrations reducing growth of algae and embryonic development of oysters by 50 percent (EC50). Toxicity tests with crustaceans and fishes were flow-throughs that estimated the measured concentration in water lethal to 50 percent (LC50). Ninety-five percent confidence limits are in parentheses.

Organims	Temperature, °C	Salinity, °/oo	Exposure Duration, Days	EC50/LC50, μg/ℓ
Algae				
Chlorococcum sp.	20	30	7	350 (270-400)
Dunaliella tertiolecta	20	30	7	580 (510-640)
Nitzschia sp.	20	30	7	600 (530-660)
Thalassiosira pseudonana	20	30	7	600 (500-700)
Mollusk				
Crassostrea virginica	20	21	2	66 (60-74)
Crustaceans				
Callinectes sapidus	19	20	4	>210
Mysidopsis bahia	26	13	4	10 (8.1-12)
Palaemonetes pugio	20	16	4	120 (100-170)
Fishes				
Cyprinodon variegatus	18	15	4	70 (56-99)
Leiostomus xanthurus	25	18	4	6.6 (5.3-8.8)

Table 2. Effect of Kepone on the survival of *Mysidopsis bahia* and on average number of young per female in a 19-day flow-through toxicity test.

Average Measured Kepone Concentration (μg/ℓ)	Percentage Survival	Number of Young per Female
Control	91	15.3
0.39	84	8.9*
1.6	50	0
4.4	3	-
8.7	0	-

*Statistically significant at $\alpha=0.05$ using 2 sample t-test.

Table 3. Effect of Kepone on and accumulation of Kepone by adult sheepshead minnows exposed for 28 days.

Average Measured Exposure Concentration, μg/ℓ	Percentage Mortality	Whole Body Concentration, μg/g
ND*	5	ND
0.05	5	0.30
0.16	0	0.78
0.80	22	3.0
1.9	80	12.
7.8	100	
24.	100	

*ND = Kepone not detected in control water (<0.02 μg/ℓ) nor in control fish (<0.02 μg/g).

Table 4. Mortality in progeny of adult sheepshead minnows that were exposed to Kepone and in progeny of unexposed, control fish. Nominal exposure for the 28-day exposure of adult fish and the 36-day exposure of progeny were the same. Progeny exposure began with embryos and ended with juvenile fish from the embryos. Residues are concentrations of Kepone (μg/g) in whole juveniles, wet weight.

Measured Exposure	Parental Fish History			
Concentration	Progeny of Unexposed Parents		Progeny of Exposed Parents	
μg/ℓ	Mortality %	Residue μg/g	Mortality %	Residue μg/g
Control (ND)	10	ND[1]	10	ND[1]
0.08	22	1.1	9	1.6
0.18	12	1.4	18	1.0
0.72	28	2.6	18	1.9
2.0	40	7.8	62	8.4
6.6	40	22.	-	-
33.	100	-	-	-

[1] ND = not detectable, <0.02 μg/ℓ, 0.02 μg/g.

Kepone in water affected progeny of exposed parents to a greater extent than progeny of unexposed parents (Table 4). Some embryos exposed to 2.0 μg/ℓ developed abnormally and fry had more pronounced symptoms and they began to die 10 days earlier when parental fish had been exposed to 1.9 μg/ℓ than was observed in progeny from unexposed parents.

Kepone also affected growth of sheepshead minnows in the 36-day exposure of progeny (Figure 1). The average standard length of juveniles exposed to all Kepone concentrations was less than that of unexposed control juveniles. Lengths decreased in direct proportion to increasing Kepone concentrations in water and were generally not influenced by parental exposure. A similar decrease was also noted in weights, but because juveniles exposed to 0.72, 2.0, or 6.6 μg/ℓ were edematous, they weighed more than unexposed juveniles of similar lengths.

Kepone was bioconcentrated by sheepshead minnow adults and their progeny exposed to the insecticide in water. Kepone was bioconcentrated in adult fish in direct proportion to concentration in exposure water (Table 3). Concentration factors averaged 5,200 (range 3,100 to 7,000). Kepone concentrations in females and their eggs were similar and were 1.3 times greater than amounts in males. Concentrations of Kepone in juvenile fish, at the end of the 36-day progeny exposure, increased with increased concentration of Kepone in water (Table 4). Prior exposure of parental fish apparently did not affect final Kepone concentration in progeny. Concentration factors for juvenile fish averaged 7,200 (range 3,600 to 20,000) and increased with decrease in concentration of exposure.

In our tests, Kepone was acutely toxic to, and accumulated by, estuarine algae, mollusks, crustaceans, and fishes. Chronic toxicity tests with *M. bahia* and *C. variegatus* revealed that Kepone affected survival, growth, and reproduction. Effects on growth were observed at one one-thousandth of the 96-hour LC50. Accumulation of Kepone was also greatest in chronic tests. Therefore, chronic tests should be used to assess Kepone's environmental hazard and to make decisions necessary to minimize its future impact on the aquatic environment.

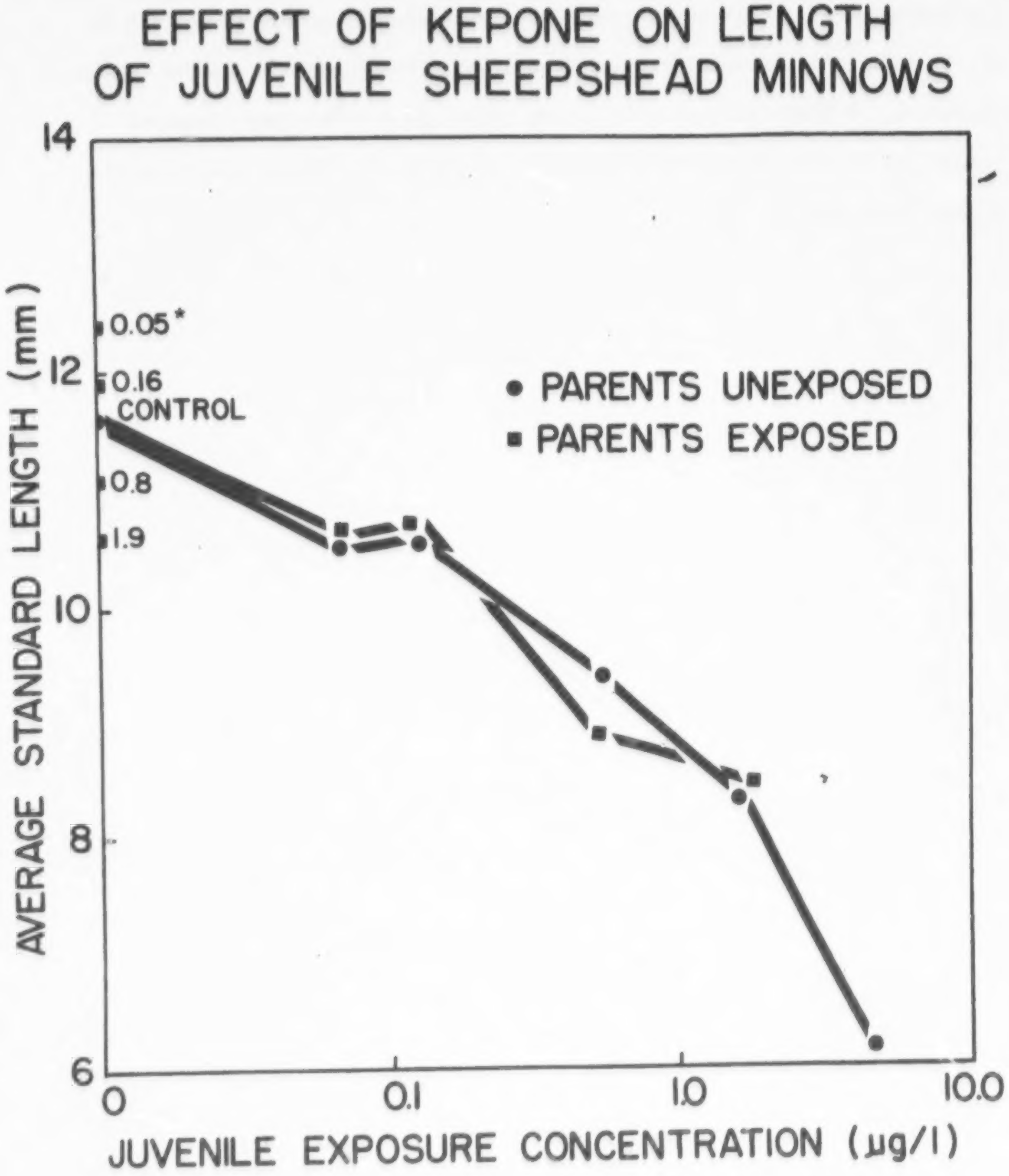

Figure 1. Average standard length of juvenile sheepshead minnows exposed as embryos, fry, and juveniles for 36 days to 0, 0.08, 0.18, 0.72, 2.0, or 6.6 µg of Kepone/ℓ of water. Parent fish in some instances also were exposed to similar concentrations of Kepone: 0, 0.05, 0.16, 0.80, or 1.9 µg/ℓ.

*Concentration of Kepone in water, µg/ℓ, for parent fish exposed prior to placement of their embryos in Kepone-free water.

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ACUTE TOXICITY OF KEPONE TO FOUR ESTUARINE ANIMALS

Schimmel, S. C. and Wilson, A. J.

ABSTRACT

Recent contamination of the James River estuary Virginia, with Kepone prompted acute flowthrough bioassays to determine the 96hour toxicity of the insecticide to four estuarine species native to that ecosystem. The species and their 96-hour LC50 values were: grass shrimp (_Palaemonetes pugio_), 121 μg/ℓ; blue crab (_Callinectes sapidus_), 210 μg/ℓ; sheepshead minnow (_Cyprinodon variegatus_), 69.5 μg/ℓ; and spot (_Leiostomus xanthurus_), 6.6 μg/ℓ. Surviving animals were analyzed for Kepone. Average bioconcentration factors (the concentration of Kepone in tissues divided by the concentration of Kepone measured in seawater) were: grass shrimp, 693; blue crab 8.1; sheepshead minnow, 1,548; and spot, 1,221.

INTRODUCTION

Few published data are available on Kepone toxicity to estuarine animals. Butler (1963) reported EC50 values (based on mortality or loss of equilibrium in 48 hours for shrimp and on inhibition of shell deposition in 96 hours for oysters) of 85 μg/ℓ for brown shrimp (*Penaeus aztecus*); 57 μg/ℓ and 15 μg/ℓ for eastern oysters (*Crassostrea virginica*) exposed at seawater temperatures of 14°C and 31°C, respectively. Twenty percent of the blue crabs (*Callinectes sapidus*) exposed to 1,000 μg/ℓ Kepone died in 48 hours. Butler's data were derived from flow-through bioassays and based on nominal, not measured, concentrations of Kepone in seawater.

Recent discharge of the insecticide, Kepone^R, into the James River estuary, Virginia has resulted in contamination of that system's water, sediment, and biota. This contamination raised questions about the acute and chronic effects of Kepone on the aquatic life in the estuary and the potential danger to humans by eating contaminated animals.

In January 1976, we initiated flow-through bioassays to determine bioconcentration and acute toxic effects of Kepone on representative species found in the James River estuary. These were grass shrimp (*Palaemonetes pugio*), blue crab (*Callinectes sapidus*), sheepshead minnow (*Cyprinodon variegatus*), and spot (*Leiostomus xanthurus*).

METHODS AND MATERIALS

Acute toxicity was determined by exposing 20 animals per aquarium to different concentrations of Kepone for 96 hours in flow-through bioassays similar to those described by Lowe et al. (1972). All test animals were acclimated to laboratory conditions for at least ten days prior to testing. The temperature and salinity of seawater in which they were held were allowed to vary with those of Santa Rosa Sound, Florida during acclimation and testing. Our acclimation and testing procedures were compatible with those of Standard Methods (A.P.H.A., 1971). All test animals were captured in the vicinity of the Gulf Breeze Laboratory and samples contained no detectable Kepone (<0.02 μg/g). During acclimation test animals were fed frozen brine shrimp daily. Animals were not fed during the tests, but could obtain food (plankton and other particulate matter) from the unfiltered seawater. Seawater was pumped from Santa Rosa Sound into a constant-head trough in the laboratory and delivered to each 18 aquarium by a calibrated siphon that delivered approximately 68ℓ/hr. One control and five experimental aquaria were used in each test. Stock solutions of Kepone (88% pure), in reagent-grade acetone, were metered into experimental aquaria at the rate of 60 mℓ/hr.

The 96-hour LC50 values were determined for both nominal and measured concentrations of Kepone in seawater. Nominal concentrations were those calculated to be in seawater, based on the concentration of the stock solution, plus the stock solution and seawater flow rates. The LC50 values were based on measured Kepone concentrations determined by chemical analysis of the exposure water. Mortality data were subjected to probit analysis to determine LC50 values and their 95% confidence limits (Finney, 1971).

At the end of each 96-hour test, surviving animals from each concentration were sacrificed, rinsed with acetone, and pooled as a single sample for residue analysis.

Water samples were analyzed by extracting one liter of seawater twice with 100 ml of methylene chloride. The combined extracts were concentrated to about 5 ml in a Kuderna-Danish Concentrator on a steam table. Fifteen milliliters of benzene were added and the extract reconcentrated to remove the methylene chloride. The extract was cleaned up on a Florisil Column as described below.

Tissues of shrimp, crabs, or fish were weighed in 150 mm x 25 mm (O.D.) screw-top test tubes and extracted twice with 5 ml volumes of acetonitrile for 30 seconds with a model PT 10-ST Willems Polytron (Brinkman Instruments, Westbury, New York). The mixture was centifuged and the acetonitrile transferred to a 250-ml separatory funnel. After the second extraction, the tissue was extracted with one 5-ml and one 10-ml volume of acetone. After each acetone extraction the tube was centrifuged and the acetone added to the 250-ml separatory funnel. To the combined extracts, 100 ml of 2.0% aqueous sodium sulfate and 10 ml of 1:1 diethyl ether-petroleum ether were added. The separatory funnel was shaken for one minute. After the solvent phases had separated, the lower aqueous phase was drained into a 250-ml beaker and the upper ether layer was collected in a 25-ml Kuderna-Danish concentrator tube. The ether extraction was repeated three times with 5 ml of 1:1 diethyl ether-petroleum ether. The combined extracts were concentrated just to dryness by placing the concentrator tube in a water bath at 45oC and blowing off the solvent with a gentle stream of nitrogen. The residue was transferred to a 200 mm x 9 mm (I.D.) Chromaflex column (Kontes Glass Co.) containing 2.3 gm of Florisil topped with 2.0 gm of anhydrous sodium sulfate. The column initially was washed with 10 ml of hexane and the residue transferred with four 0.5 ml volumes of 5% diethyl ether in hexane. The column was eluted with 20 ml of 5% diethyl ether in hexane to remove PCB and pesticides. Kepone was eluted in a second elution of 40 ml of 1% methanol in benzene. Extracts were concentrated or diluted to appropriate volumes for analyses by electron capture gas chromatography.

Determinations were obtained by Varian Aerograph Model 2100 and 1400 Gas Chromatographs equipped with 182 cm x 2 mm (I.D.), glass columns packed with 2% SP2100 and 9.75% SP2250: 9.97% SP2401 on 100/120 mesh Supelcoport. The operating parameters were: oven temperature 185°C, injector temperature 200°C, detector temperature 216°C, and nitrogen carrier gas flow rate 25 ml/ℓ minute.

The average recovery rate of Kepone from fortified tissue was 87%; from water, 85%. Residue concentrations were calculated on a wetweight basis without a correction factor for percentage recovery. All samples were fortified with an internal standard (dichlorobenzophenone) prior to analysis to evaluate the integrity of the results.

RESULTS AND DISCUSSION

Kepone, at concentrations tested, was acutely toxic to shrimp and fishes but not to blue crabs. The LC50 values varied widely among species. Spot were the most sensitive with a 96-hour LC50 of 6.6 μg/ℓ; the sheepshead minnow LC50 was over ten times higher (69.5 μg/ℓ). The two crustaceans were less sensitive. Grass shrimp LC50 was 120.9 μg/ℓ, and no significant mortality was observed in blue crabs measured concentrations as high as 210 μg/ℓ (Tables 1 and 2).

Although the sensitivity of fish to Kepone toxicity differed, the symptoms of Kepone poisoning were similar. An early symptom was lethargic behavior followed by loss of equilibrium. These symptoms occurred in sheepshead minnows at 48 hours in 56 and 100 μg/ℓ concentrations and 96 hours in 18 and 32 μg/ℓ concentrations. Spot exhibited the symptoms in 48 hours when exposed to 7.5, 13.5 and 24 μg/ℓ Kepone. An advanced stage of poisoning was evident in dark coloration of portions of the fish's body. This color change was striking in that some fish had normal coloration on one side of their bodies, while the other side was nearly black with a sharp line of demarcation. Some spot and sheepshead minnows were darkened in only one quadrant of the body; for example, the left side posterior to the pectoral fins. These color changes were always more marked and appeared earlier in the higher Kepone concentrations. Hansen et al. (In press) also noted color changes in sheepshead minnows exposed to a lower Kepone concentration (0.8 μg/ℓ) over a longer duration (11 days). The same authors also noted that growth, reproduction and survial of sheepshead minnows were affected in 36 days by Kepone concentrations as low as 0.08 μg/liter, which is 0.001 of our sheepshead minnow (LC50 (69.5 μg/liter). If we assume that the same ratio exists for spot as Hansen et al. reported for sheepshead minnows, then the no-effect level for spot would be less than 0.007 μg/liter based on our spot LC50 (6.6 μg/liter).

No color changes were observed in the two crustaceans although they were lethargic in Kepone concentrations greater than 75 μg/liter.

Kepone was bioconcentrated by all test animals in 96 hours, although bioconcentration factors (concentration of Kepone in tissue divided by measured Kepone in water) varied from species to species (Table 1). (The bioconcentration factors for fish were similar, $\bar{x}$ = 1200-1500). The two fishes bioconcentrated averages of 1.7 and 2.3 X the bioconcentration factor of the grass shrimp and 150 and 190 X that of the blue crab. This difference has been noted in similar bioassays with other organochlorine insecticides. Schimmel _et_ _al_. (1976) reported that sheepshead minnows, spot and pinfish (_Lagodon_ _rhomboides_) bioconcentrated 4 to 70 X more heptachlor than grass shrimp or pink shrimp (_Penaeus_ _duorarum_). A similar relationship occurred when some of the same species were exposed to toxaphene (Schimmel _et_ _al_.. In press) and dieldrin (Parrish _et_ _al_., 1974) in 96-hour bioassays. The reason for an extremely low bioconcentration factor in the blue crab compared to grass shrimp is not known.

Further studies over a longer period of time are required to better understand the more subtle effects of Kepone on estuarine animals. One reason for this assessment is that most deaths occurred after 48 hours in our tests. These studies should include: (1) long-term bioconcentration studies; (2) bioassays which include the hatching and early development of an estuarine animal; and (3) studies to determine movement of Kepone through an estuarine food web.

Table 1. Toxicity of Kepone to and uptake by four estuarine organisms after 96 hours exposure.

SPECIES	WATER CONCENTRATION (μg/ℓ) DESIRED	WATER CONCENTRATION (μg/ℓ) MEASURED	MORTALITY (%)	WHOLE-BODY RESIDUE (μg/g wet weight)	BIOCONCENTRATION FACTOR
Grass Srhimp (Palaemonetes pugio)	Control	ND[1]	0	ND[1]	--
	13.5	12.	0	5.1	425
	24.	15.	0	14.	933
	42.	39.	0	29.	744
	75.	69.	5	42.	609
	135.	121.	50	94.	777
					$\bar{x}$ = 698
Blue Crab (Callinectes sapidus)	Control	ND	0	ND	--
	42.	--	0	--	--
	75.	--	10	--	--
	135.	110.	5	0.85	7.7
	187.	164.	0	1.7	10.4
	240.	210.	0	1.3	6.2
					$\bar{x}$ = 8.1
Sheepshead Minnow (Cyprinodon variegatus)	Control	ND	0	ND	--
	10.	7.1	0	11.2	1577
	18.	14.	0	20.9	1493
	32.	23.	5	44.4	1930
	56.	51.5	20	63.6	1235
	100.	78.5	65	118.4	1506
					$\bar{x}$ =1548
Spot (Leiostomus xanthurus)	Control	ND	0	ND	--
	2.4	1.5	5	1.7	1133
	4.2	3.4	10	3.2	941
	7.5	4.4	45	7.0	1591
	13.5	7.8	40	10.8	1385
	24.	15.9	95	16.8	1057
					$\bar{x}$ =1221

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[1] ND - non detectable; <0.02 μg/ℓ in water, <0.02 μg/g in tissue.

Table 2. 96-hour toxicity of Kepone to several estuarine animals in flowing seawater bioassays. The 95% confidence intervals are in parentheses. Animal sizes are rostrum-telson length for shrimps, carapace width for crabs, and standard length for fishes.

SPECIES	SIZE ($\bar{x}$, mm)	NOMINAL 96-HOUR LC50 in μg/ℓ (95% CONFIDENCE LIMIT)	MEASURED 96-HOUR LC50 in μg/ℓ (95% CONFIDENCE LIMIT)	TEMPERATURE ($\bar{x}$, °C)	SALINITY ($\bar{x}$, °/oo)
Grass Shrimp (*Palaemonetes pugio*)	27.8	134.8 (114.1-193.9)	120.9 (103.0-171.6)	20.0	16.0
Blue Crab (*Callinectes sapidus*)	34.3	>240	>210	19.0	20.0
Sheepshead Minnow (*Cyprinodon variegatus*)	20.0	83.0 (67.9-115)	69.5 (56.3-99.5)	18.0	15.0
Spot (*Leiostomus xanthurus*)	33.9	10.5 (8.3-14.0)	6.6 (5.3-8.8)	25.0	18.0

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KEPONE ACCUMULATION AND FOOD CHAIN TRANSFER

L.H. Bahner, A.J. Wilson, J.M. Sheppard, J.M. Patrick, L.R. Goodman, and G.E. Walsh

ABSTRACT: Accumulation, transfer, and loss of Kepone in estuarine organisms were studied in laboratory bioassays. Kepone was bioconcentrated by oysters (Crassostrea virginica), mysids (Mysidopsis bahia), grass shrimp (Palaemonetes pugio), sheepshead minnows (Cyprinodon variegatus), and spot (Leiostomus xanthurus), from concentrations as low as 0.023 µg/ℓ seawater. Bioconcentration factors ranged from 10 to 340 in static exposures and 900 to 13,500 in flow-through bioassays and were dependent on species and exposure duration.

Depuration of Kepone from oysters in Kepone-free water was rapid (35% loss in 24 hours); however, depuration of Kepone was slow in crustaceans and fish, with tissue concentrations decreasing 30-50% in 24-28 days.

Oysters, fed Chlorococcum containing approximately 34 µg Kepone/g wet weight, attained 0.21 µg Kepone/g (wet tissue) in 14 days, but when fed Kepone-free plankton, depurated Kepone to below detectable concentrations (<.02 µg/g) within 10 days.

Spot obtained Kepone when fed live mysids that had grazed on Kepone-laden brine shrimp. Kepone residues (1.05 µg/g wet tissue) in these fish approached the concentration of their food (1.23 µg/g wet tissue); at the lower concentration tested, Kepone concentrations below detection limits (<.2 µg/g) in prey accumulated in the predator to detectable concentrations (0.02 µg/g) within 30 days. Bioaccumulation factors (concentration of Kepone in predator/concentration in prey) at 30 days were equal (0.85 spot/mysid; 0.53 mysid/brine shrimp)in the high and low concentrations tested.

Introduction

Contamination of the James River water, sediments, and biota with Kepone has prompted research to help define the routes of transfer of the insecticide from water through selected estuarine trophic levels. Biota of the James River Estuary and Chesapeake Bay contain Kepone (Hansen et al. 1976), apparently due to transport of the chemical downstream from the freshwater portion of the river. Since no convenient method existed to assess the rate of Kepone movement in the biota of the James River and Chesapeake Bay, laboratory bioconcentration from water and bioaccumulation from food experiments were designed to determine the rates and magnitudes of Kepone accumulated from water and food by selected estuarine organisms. It is important to determine the accumulation of Kepone from water and food by various estuarine species, so that the information can be used in the decision-making processes that may affect the water quality for the biota in the Chesapeake Bay region or limit transfer of Kepone to seafoods consumed by man. The alga, oyster, mysid, shrimp, and fish used in our experiments are representative of many ecologically important species. The top consumers in our food chains tested are endemic to both the Chesapeake Bay area and northern Gulf of Mexico and are commercially important human food items. Leiostomus xanthurus, the top carnivorous species of one laboratory food-chain, provides an estimated 21.5 million pounds annual recreational catch for fishermen of the Middle Atlantic states (U.S. Department of Commerce 1975).

This study provides information about: (1) the rates and magnitudes of Kepone accumulation from water by estuarine biota; (2) rates of Kepone depuration by animals in Kepone-free water; and (3) rates of Kepone transfer through laboratory food chains.

Methods

BIOCONCENTRATION OF KEPONE FROM WATER BY ESTUARINE ORGANISMS

Oysters

Eastern oysters (Crassostrea virginica) were exposed to Kepone (88% pure) in a 56-day flow-through bioassay to determine the rates of uptake and depuration of this insecticide. Seawater (mean temperature 14.2 C; mean salinity 15 °/oo) was pumped from Santa Rosa Sound, Florida, into a constant-head trough in the laboratory. Approximately 440 ℓ/hour was delivered by siphons to each of three 166 ℓ aquaria. Oysters (100/aquarium) were not fed but could obtain plankton from the unfiltered seawater in which they were held. Stock solutions of Kepone in triethylene glycol (TEG) were metered into the two experimental aquaria at the rate of 10 ml/day. Measured concentrations of Kepone in the two experimental aquaria were 0.39 and 0.03 μg/ℓ seawater. A control aquarium received 10 ml TEG/day.

Oysters (56 mm to 92 mm, umbo to distal valve edge height; $\overline{x}$ = 71.8 mm) were collected, acclimated to laboratory conditions for ten days, exposed to Kepone for 28 days, and then held for 28 days in Kepone-free seawater. Five oysters were sampled from each aquarium at 4 hours, 8 hours, 1 day, 8 days, and twice weekly thereafter to day 28. During the 28-day depuration portion of the test, oysters were sampled at similar intervals. Analysis methods for Kepone in water and tissues (whole-body, wet weight) were those of Schimmel and Wilson (in press).

Crustaceans

Mysids (Mysidopsis bahia), collected from laboratory cultures (Nimmo et al. in press), were exposed to average measured concentrations of 0.026

or 0.41 μg Kepone/ℓ seawater for 21 days (mean temperature 27.2 C; mean salinity 18 °/oo) and in a second experiment, grass shrimp (Palaemonetes pugio), seined and acclimated to experimental conditions for 10 days, were exposed to average measured concentrations of 0.023 or 0.40 μg Kepone/ℓ seawater in a 28-day flow-through bioassay (mean temperature 27 C; mean salinity 25 °/oo). Experimental methods used were those of Bahner et al. (1975). The grass shrimp were held for an additional 28-day period in clean seawater to assess depuration of the insecticide. Filtered seawater at a rate of approximately 60 ℓ/hour flowed through each aquarium containing mysids or grass shrimp. Mysids and shrimp were fed 48-hour-old Artemia nauplii daily. Kepone content of mysids and shrimp was determined weekly during exposure and depuration. In a third experiment, grass shrimp were collected by seine from the Lafayette River estuary near Norfolk, Virginia, and were held in flowing seawater (mean temperature 25.5 C; mean salinity 15 °/oo) in the laboratory to determine the extent of depuration of Kepone from field-exposed shrimp. These shrimp were analyzed for Kepone concentrations on days 7, 11, 17, and 21 after being transferred to flowing Kepone-free water in our laboratory.

Fishes

Sheepshead minnow (Cyprinodon variegatus) adults, acclimated to laboratory test conditions, were exposed to an average measured concentration of 0.05 μg Kepone/ℓ of water (mean temperature 30 C; mean salinity 15 °/oo) for 28 days, using the methods of Hansen et al. (in press) and were held in Kepone-free water for an additional week. Ten fish, generally five females and five males, were sampled on days 0,1,3,7,14,21, and 28 of exposure to Kepone and on day 7 of depuration.

Spot (*Leiostomus xanthurus*) were seined, acclimated for 10 days, exposed to average measured concentrations of 0.029 or 0.4 μg Kepone/ℓ of filtered flowing seawater (mean temperature 23 C; mean salinity 18 $^o/oo$) for 30 days and allowed to depurate the chemical for 24 days. Composite samples of three fish were sampled each week for residue analysis. Spot, exposed to 0.4 μg Kepone/ℓ seawater and allowed to depurate for 24 days, were dissected into liver, brain, gills, muscle, and offal (rest of body tissues) and analyzed for Kepone.

Fillets (including scaleless skin) and the remaining portions of sheepshead minnows and spot (wet weight) were analyzed for Kepone content. The data were summed to calculate concentrations in whole fish.

BIOACCUMULATION OF KEPONE IN FOOD CHAINS CONSISTING OF ESTUARINE ORGANISMS

Algae-Oyster Food Chain

The green alga, *Chlorococcum* sp., contaminated with Kepone was used as food for oysters to determine if contaminated phytoplankton could be a significant source of the pesticide to oysters. *Chlorococcum* sp. was grown for 6 days in one liter of culture medium in 2800-ml Fernbach flasks according to the method of Hollister et al. (1975). Random cultures were dosed with 0.1 mg Kepone in acetone, while others served as controls after treatment with acetone alone. After 24 hours of exposure, algal cultures were harvested by centrifugation and washed three times by resuspension in clean growth medium and centrifugation. The cells were resuspended in 5ℓ of seawater and fed to oysters by using the methods of Bahner and Nimmo (1976). Samples of the algae were analyzed daily for Kepone.

Rate of Kepone accumulation was determined by allowing oysters to feed on control or Kepone contaminated green algae in flowing seawater. Oysters for this study were collected and acclimated for 10 days to laboratory conditions in flowing seawater. Twenty-four oysters were placed in each of two aquaria (one control and one experimental) that received 60ℓ filtered seawater/hour (mean temperature 22 C, mean salinity 19 $^{o}/oo$) and were fed approximately 50 mℓ of the appropriate (control or contaminated) algal suspension at 15-minute intervals for 14 days. A 10-day depuration period followed the feeding study during which the oysters received raw, unfiltered flowing seawater and no additional Chlorococcum. Oysters (n = 3 per sample) were analyzed for Kepone content on days 0,7,10,14,17, and 24 of the experiment.

Plankton-Mysid-Fish Food Chain

Transfer of Kepone from water to plankton to mysids to fish was investigated by feeding living brine shrimp nauplii that were contaminated with 2.33 μg Kepone/g tissue to mysids, that were then fed to spot, the top predator of this laboratory food chain. Juvenile spot were seined and acclimated according to the methods previously described for sheepshead minnows and spot. Mysids (Mysidopsis bahia), the intermediate food organism, were collected from laboratory cultures. Commercially available brine shrimp eggs were hatched during 48 hours in clean seawater or in seawater to which 0.005 or 0.1 mg Kepone/ℓ was added (Bahner and Nimmo 1976). The brine shrimp were harvested daily and served as the "planktonic" food for the mysids. Approximately 40 mysids were distributed among each of six compartments of two 30-ℓ aquaria. The compartments were separated by coarse nylon screen that allowed for flow of water and Artemia throughout each aquarium while confining the mysids to separate compartments. Mysids that had fed on Artemia for 72 hours were harvested from one compartment of each holding aquarium, rinsed with seawater, and fed to the spot. Each compartment was refilled with mysids to provide for subsequent feeding periods. By this method, each of 12 juvenile spot, (average length 40 mm), in each of three 30-ℓ glass aquaria, were fed 3 to 5 control or contaminated mysids daily. Aquaria containing spot received 60ℓ of seawater/hour to prevent anoxia and to minimize bioconcentration of Kepone depurated from the mysids. Water averaged 19 C and 18 ^{o}/oo salinity. Brine shrimp, 30 to 45 mysids, 2 to 3 spot, and water from each aquarium were analyzed weekly for Kepone.

Results and Discussion

BIOCONCENTRATION FROM SEAWATER

Kepone was bioconcentrated from water by oysters, mysids, grass shrimp, sheepshead minnows, and spot in all concentrations tested (Figs. 1, 2, 3, 4, and 5; Table 1) and all species showed nearly equilibrated tissue concentrations of Kepone within 8 to 17 days after exposure to Kepone began in water. Bioconcentration factors for Kepone in these species ranged from 2,300 to 13,500 in long-term (>96 hrs) flow-through bioassays (Table 2). Kepone bioconcentrated in oysters to approximately 10,000 times the concentration in the exposure water within 19 days. Mysids bioconcentrated Kepone up to 13,000 times the amount measured in the exposure water. Each mysid (mean live-weight = 2.5 mg for 66 adults), exposed to 0.026 μg Kepone/ℓ for 14 days contained approximately 5.9 ng Kepone; therefore this amount of the chemical could enter food chains of estuarine predators that consumed each mysid. Stomachs of flounders from Chesapeake Bay (standard length 25 to 174 mm) contained an average of twenty mysids (Stickney et al. 1974); mysids comprised up to 14% of the diets of striped bass from the York and Rappahannock Rivers. Mysids were conspicuously absent in gut analyses of James River striped bass, but decapod crustaceans (i.e. Palaemonetes sp.) accounted for 48% (by volume) of their diets (Markel and Grant 1970). Palaemonetes have one of the highest bioconcentration factors of Kepone (Table 2), and like other decapod crustaceans, are one of the species least sensitive to acute exposures of Kepone (Schimmel and Wilson In press). Grass shrimp bioconcentrated Kepone up to 11,000 times the concentration in the exposure water. After 28 days of exposure to 0.023 μg Kepone/ℓ, each shrimp contained approximately 8.6 ng Kepone, an amount that could be transferred to predators.

Bioconcentration of Kepone was more efficient with increased concentrations in water for all crustaceans tested (Table 2).

Kepone was bioconcentrated from water by sheepshead minnows--important omnivores that link energy transfer from detritus and benthic plants and animals to carnivores in higher trophic levels. Each fish (mean weight 1.5 g) contained approximately 0.54 μg Kepone after 28 days of exposure to 0.05 μg Kepone/ℓ seawater. Kepone concentrations were slightly higher in female sheepshead minnows (0.35 μg/g) than male fish (0.25 μg/g).

Spot, a commercially valuable food fish, bioconcentrated Kepone from 0.029 μg/ℓ seawater; each fish (mean weight 1.4 g) contained approximately 0.13 μg Kepone. The bioconcentration factors for Kepone in fish were similar to those of other chlorinated hydrocarbon insecticides (Schimmel et al. 1975; Schimmel et al. 1976). Kepone accumulated in edible fillets to near the whole-body concentrations in fish (Figs. 4, 5, & 6); therefore, one of the largest reserves (22 °/o) of Kepone in absolute weight is in the edible portion of contaminated fish. Although the greatest body burdens of Kepone on a wet-weight basis are in the brain, liver, and gill tissues, the relatively large size of muscle and offal tissues contributes large Kepone reserves to higher trophic levels (Fig. 6).

Depuration of Kepone was not consistent among the species tested. Clearance of the chemical from oysters was relatively rapid, with no Kepone detected within 7 to 20 days after exposure ceased (Fig. 1). Depuration of Kepone from laboratory exposed grass shrimp (Fig. 3) and fish (Fig. 4 & 5) was slower; Kepone concentrations were reduced 30-50 °/o in 24 to 28 days. Grass shrimp from the Lafayette River depurated Kepone at rates similar to those of laboratory exposed shrimp with approximately 20 °/o of the Kepone lost during 21 days in seawater containing no Kepone. Spot that were exposed to Kepone for 30 days and allowed to depurate for 24 days, contained highest Kepone concentrations in brain, followed by liver, gills, and and muscle (Fig. 6). Many chlorinated chemicals are highly concentrated in liver and other fatty tissues (Parrish et al. 1974; Parrish et al. 1975) but the unusual distribution of Kepone might be explained by its water solubility relative to other insecticides.

BIOACCUMULATION OF KEPONE IN FOOD CHAINS CONSISTING OF ESTUARINE ORGANISMS

Algae-Oyster Food Chain

Chlorococcum, grown in media enriched to 0.1 mg Kepone/ℓ, bioconcentrated the chemical to a mean of 34 μg/g in whole cells; the bioconcentration factor in these static exposures was 340X (Table 2). In preliminary tests, continuous infusion of 2.1 μg Képone/hour into static cultures of Chlorococcum produced cells with bioconcentration factors near 6000 x within 48 hours; adsorption of Kepone by the cells and vessels limited the average measured concentration in the media to approximately 0.04 mg/ℓ. Continuous exposure in this test is probably more representative of those occurring in an estuary and places the importance of bioconcentration of Kepone by phytoplankton in proper perspective.

Oysters bioaccumulated Kepone to 0.21 μg/g when fed Chlorococcum sp. containing an average of 34 μg Kepone/g for 14 days (Fig. 7; Table 3). Kepone in feces and pseudofeces from these oysters averaged 1.78 μg Kepone/g (dry weight). Kepone was not detectable in the unfiltered water samples; shell growth was evident; and all oysters gained weight during the test. Weight gain in exposed oysters was not different than control oysters (analysis of covariance, $\alpha = 0.05$). Kepone concentrations in oysters fed the contaminated algae appeared to almost reach equilibrium in 14 days; but quantity of Kepone transferred from these algae to oysters was limited, probably due to rapid depuration of the chemical from the oysters. Kepone was not detectable (<0.02 μg/g) 10 days after the oysters received no contaminated food. Most Kepone was depurated from oysters within 96 hours; therefore, if oysters in the natural environment contain measurable Kepone residues, a recent or continuous source of Kepone from water and/or food has been available.

The maximum overall accumulation and transfer of Kepone or food-chain factor from water to algae and finally to oysters was 2.1 (Table 4). The food-chain factor was obtained by dividing the concentration of the contaminant in the final consumer by the concentration of the contaminant in the water of the primary producer. The concentration measured in each consumer can be compared with a lower trophic level to determine the bioaccumulation factor of the contaminant for that predator-prey pair. Bioaccumulation factor is similar to bioconcentration factor, but the contaminant is in food and is consumed by the predator. The bioaccumulation factor for oysters consuming algae under these test conditions was only 0.007 (Table 4). These data indicate that transfer of Kepone from algae by oysters was inefficient, or that the uptake was masked by the oyster's ability to depurate the chemical quickly.

Plankton-Mysid-Fish Food Chain

Spot accumulated Kepone by consuming live mysids that had grazed on Kepone-laden brine shrimp (Fig. 8; Tables 3, 5). Brine shrimp exposed to 0.1 mg Kepone/ℓ seawater contained whole-body residues of 2.33 μg/g after

48 hours. Mysids that fed for 72 hours on these brine shrimp contained 1.23 μg Kepone/g. Kepone concentrations in spot that consumed the mysids for 30 days were slightly less than those in the mysids (Fig. 9), but uptake of Kepone exceeded depuration in fish as indicated by the positive slope of the uptake curves. The failure for residues to reach equilibrium during the test could be attributed to the slow depuration of Kepone from fish tissues.

Mysids, which consumed Artemia with residues of 0.05 or 2.33 μg Kepone/g (wet weight), attained 0.023 (estimated) or 1.23 μg Kepone/g whole-body residues within 72 hours. The estimated 0.023 μg Kepone/g whole-body mysids, obtained by assuming the bioaccumulation factor of 0.85 (Table 5) for Kepone transfer from mysids to fish as observed in the food chain beginning with 0.1 mg/ℓ, also occurred in the food chain that began with 0.05 mg Kepone/ℓ. The residue in mysids was then estimated to be 0.023 μg Kepone/g, which was consistent with the estimated bioaccumulation factor of 0.5 for Kepone transfer from Artemia to mysids for 72 hours. The food-chain factors were different for this food chain (3.9 compared to 10.5), since the bioconcentration factor for Kepone by brine shrimp from the lower concentration in water (0.005 mg/ℓ) was less than that from the higher concentration (0.1 mg/ℓ). The initial bioconcentration of Kepone from water by planktonic food organisms was the dominant source of Kepone to each member of this food chain, since bioaccumulation factors were less than unity.

In the field, lower concentrations of Kepone in seawater could result in a duplication of Kepone residues found in the fish of this food chain because the plankton could be expected to be chronically exposed to the contaminant. Thus, the food-chain factor would be expected to increase in the natural environment since bioconcentration factors for a chlorinated hydrocarbon pesticide (DDT) in feral plankton have been shown to exceed 4000X (Cox 1971). However, bioconcentration of Kepone could overshadow the amount of the chemical received from food by the animals in this food chain. Approximately 3,000 times as much Kepone in food as in water was needed to produce similar concentrations in spot in 28 to 30 days. Therefore, bioconcentration of Kepone was dominant in this food chain, but significant quantities (>85 °/o) of Kepone transferred from prey to predatory fish. Rapid uptake from water and food, slow depuration, and appreciable solubility in water indicate that Kepone will transfer through food webs and pose threats to consumers.

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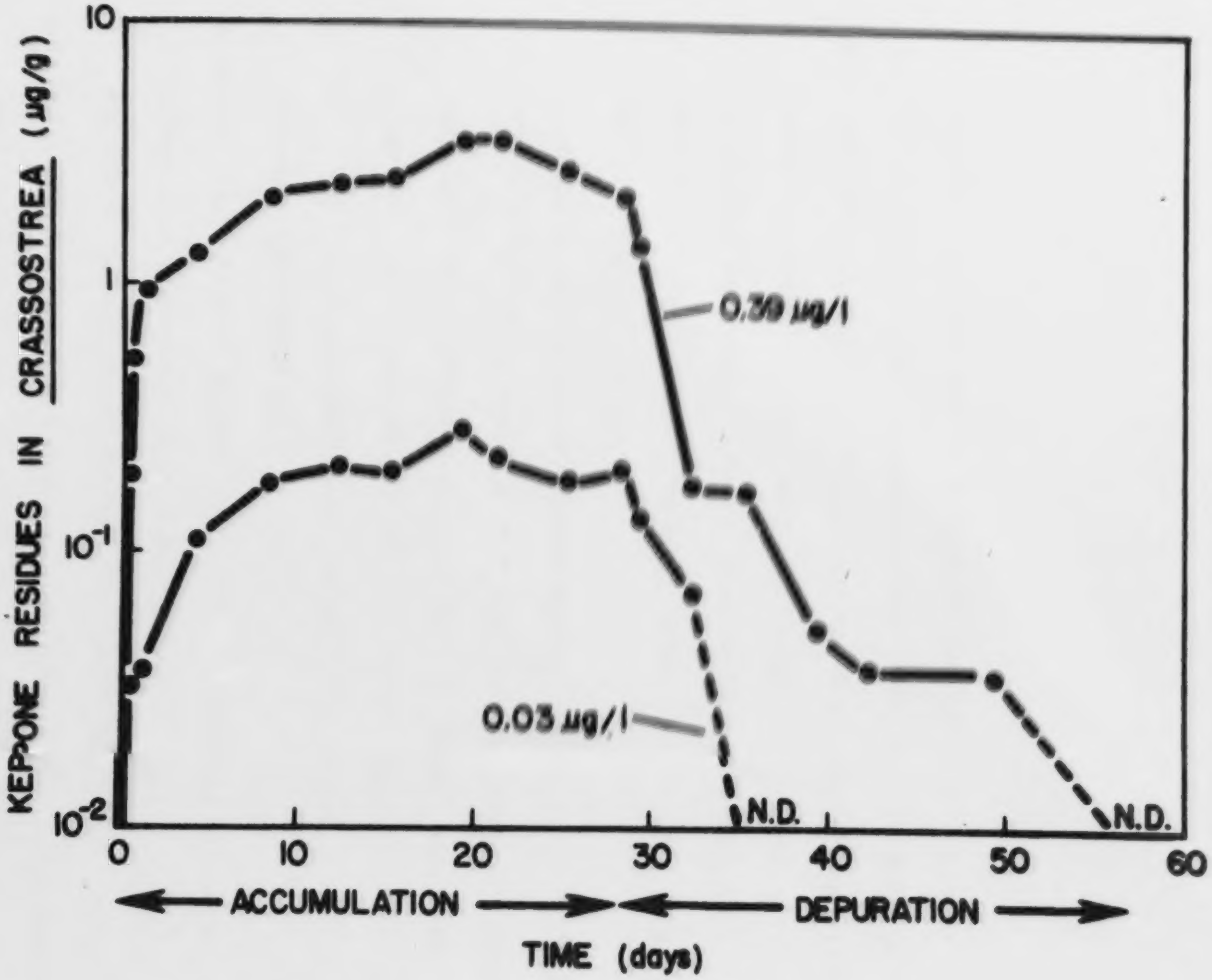


Fig. 1. Bioconcentration of Kepone from water containing average measured concentrations of 0.03 cr 0.39 µg/ℓ by oysters (Crassostrea virginica) exposed for 28 days, and its depuration by oysters placed in Kepone-free water for 28 days (mean temperature 14.2°C; mean salinity 15 ‰). ND = not detectable, <0.02 µg/g wet weight.

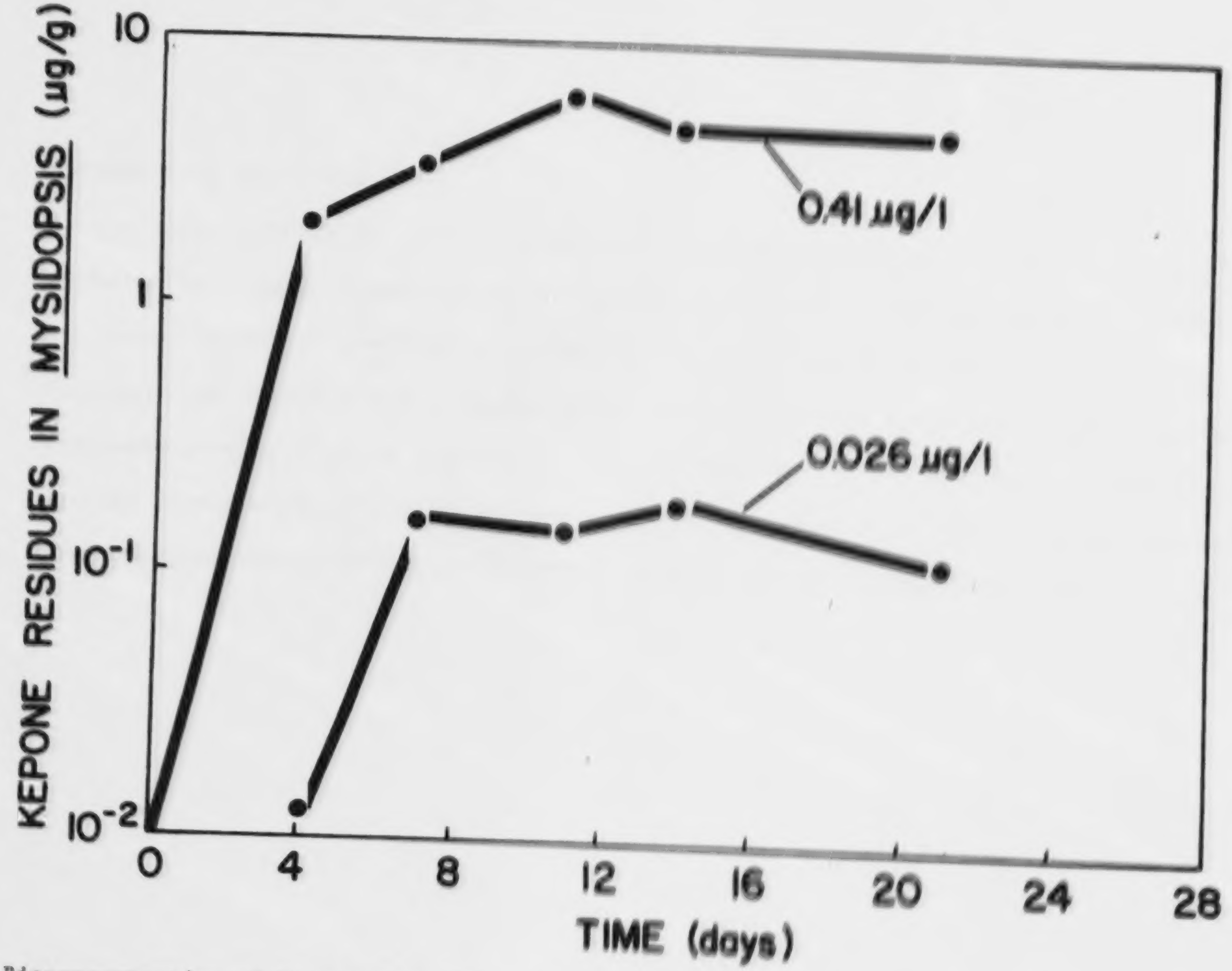
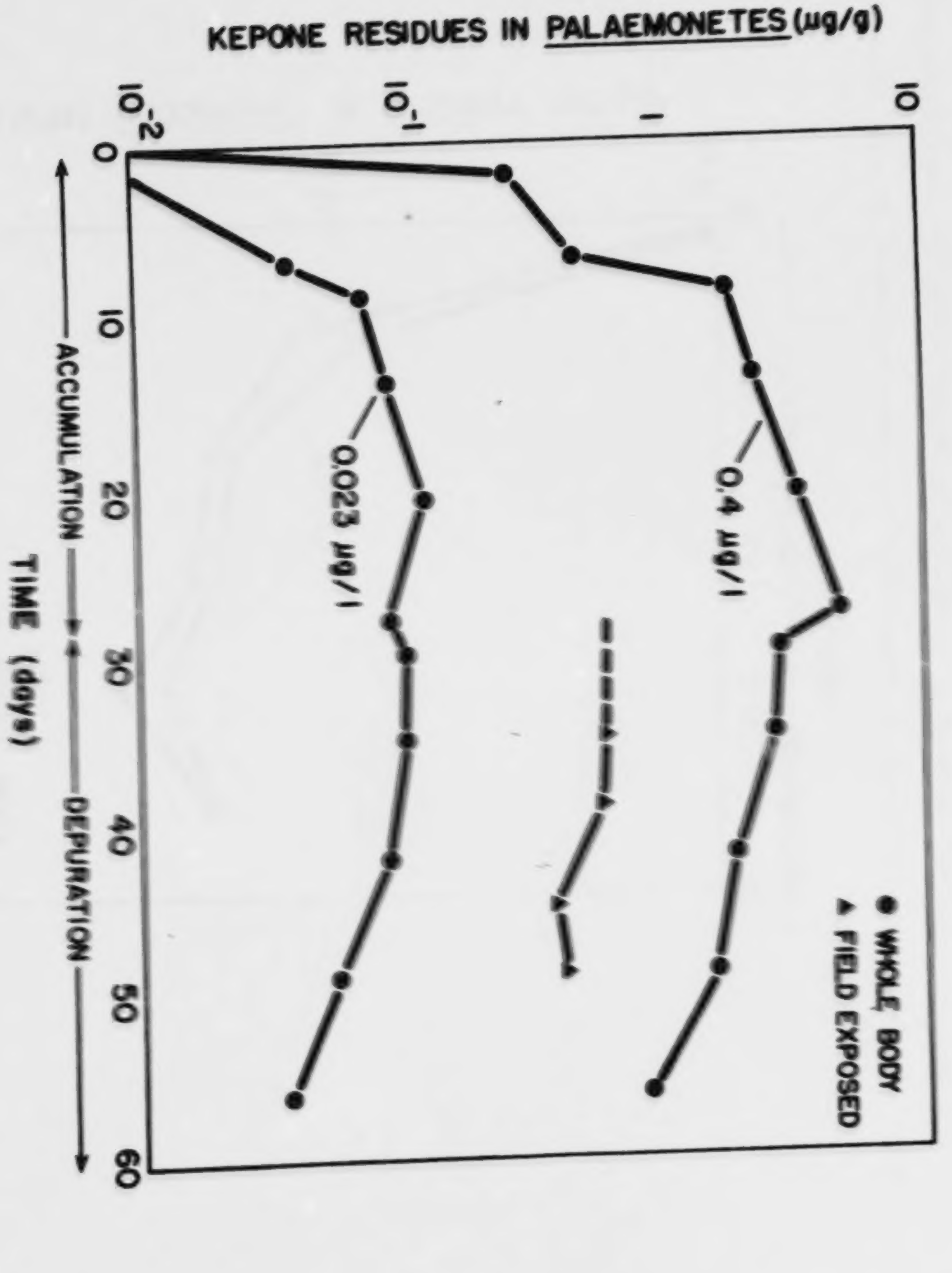


Fig. 2. Bioconcentration of Kepone from water containing average measured concentrations of 0.026 or 0.41 µg/ℓ by mysids (*Mysidopsis bahia*) exposed for 21 days (mean temperature 27.2^{0}C; mean salinity 18 ^{o}/oo).

Fig. 3. Bioconcentration and depuration of Kepone in grass shrimp (*Palaemonetes pugio*) during 56-day study. Circles indicate concentrations of Kepone accumulated from water containing average measured concentrations of 0.023 or 0.4 $\mu g/\ell$ by grass shrimp exposed in the laboratory for 28 days, and its depuration by shrimp placed in Kepone-free water for 28 days (mean temperature 27^{o}C; mean salinity 25 $^{o}/oo$). Triangles indicate concentrations in shrimp collected from Lafayette River, Norfolk, Virginia and held in clean flowing seawater at the ERL, Gulf Breeze, for 21 days (mean temperature 25.5^{o}C; mean salinity 15 $^{o}/oo$). Dashed line represents extrapolation to initial concentration at beginning of depuration.


KEPONE RESIDUES IN PALAEMONETES (µg/g)
10
1
10^{-1}
10^{-2}
0
10
20
30
40
50
60
TIME (days)
ACCUMULATION
DEPURATION
0.4 µg/l
0.023 µg/l
● WHOLE BODY
▲ FIELD EXPOSED

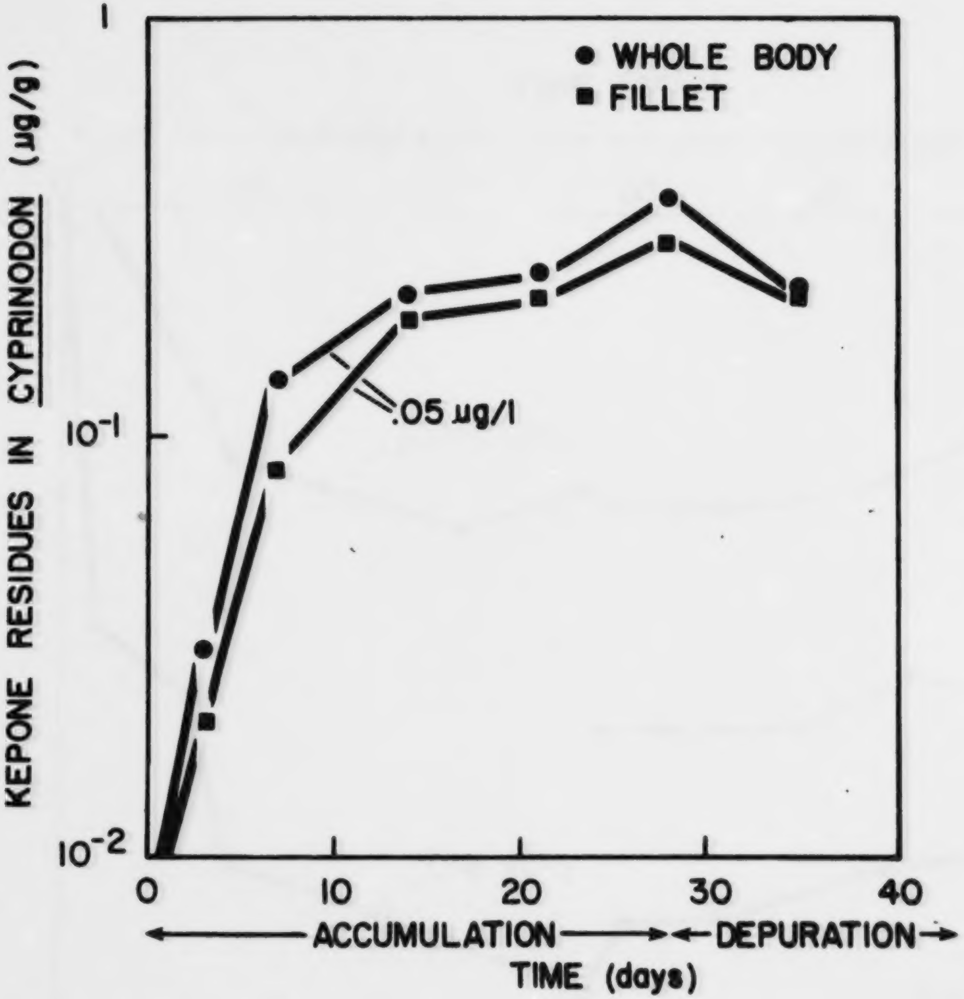


Fig. 4. Bioconcentration of Kepone from water containing average measured concentration of 0.05 µg/ℓ by sheepshead minnows (Cyprinodon variegatus) exposed for 28 days, and its depuration from fish placed in Kepone-free water for 7 days (mean temperature 30°C; mean salinity 15 °/oo).

Fig. 5. Bioconcentration of Kepone from water containing average measured concentrations of 0.029, 0.40, 1.5*, 3.4*, 4.4*, 12.0*, and 16.0* µg/ℓ by spot (Leiostomus xanthurus) exposed for 4 or 30 days, and its depuration by fish placed in Kepone-free water for 24 days (mean temperature 23°C; mean salinity 18 °/oo). *Data from Schimmel and Wilson (in press).

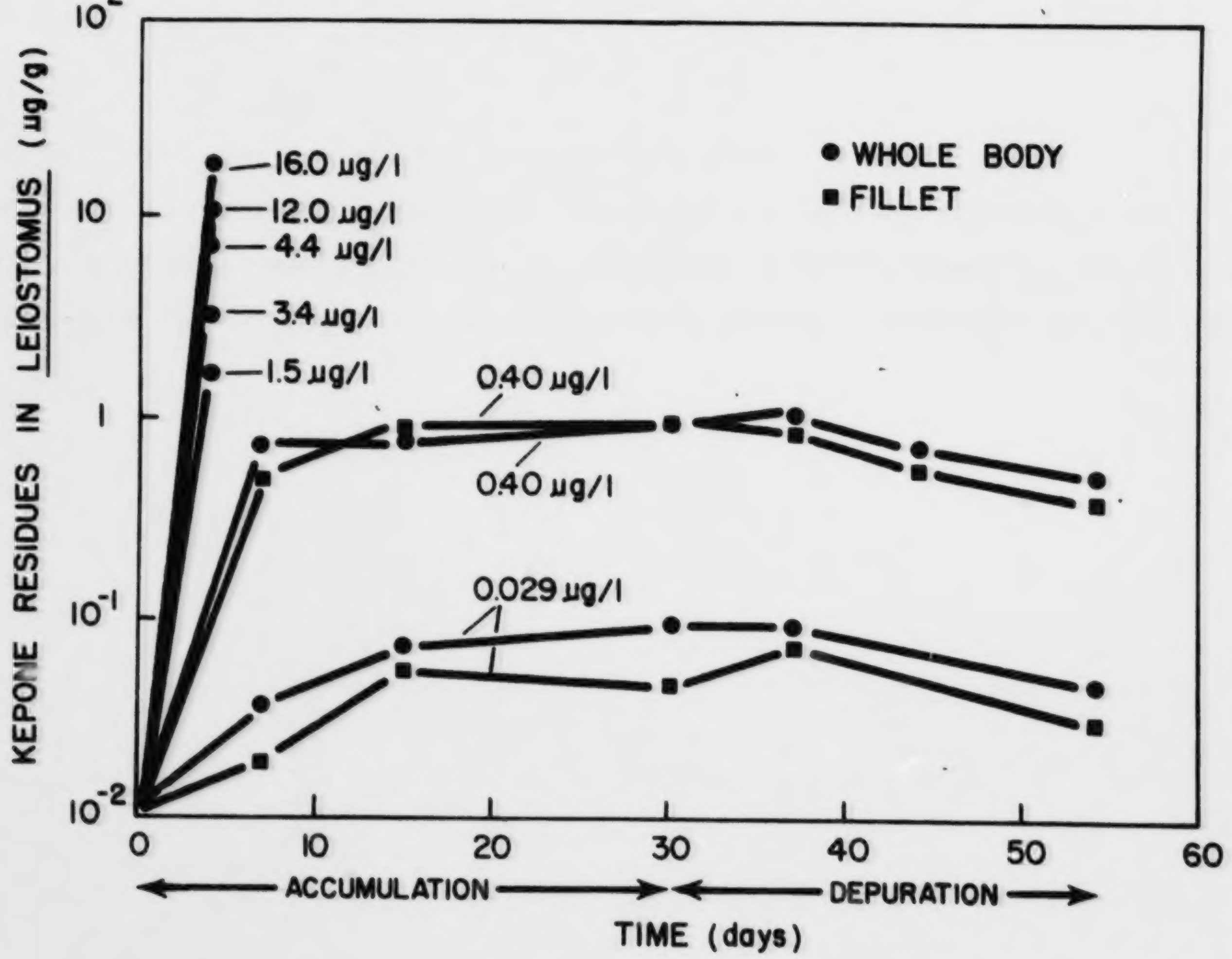

KEPONE RESIDUES IN LEIOSTOMUS (µg/g)
10^2
10
1
10^-1
10^-2
16.0 µg/l
12.0 µg/l
4.4 µg/l
3.4 µg/l
1.5 µg/l
0.40 µg/l
0.40 µg/l
0.029 µg/l
● WHOLE BODY
■ FILLET
0
10
20
30
40
50
60
ACCUMULATION
DEPURATION
TIME (days)

Fig. 6. Distribution of Kepone in selected tissues of spot (Leiostomus xanthurus). Spot were exposed to 0.4 μg Kepone/ℓ for 30 days and allowed to depurate and equilibrate for an additional 24 days prior to sampling (mean temperature 23°C; mean salinity 18 °/oo). Percentage of whole-body Kepone burden in five tissues is on left. Measured residues (wet weight) are on right.

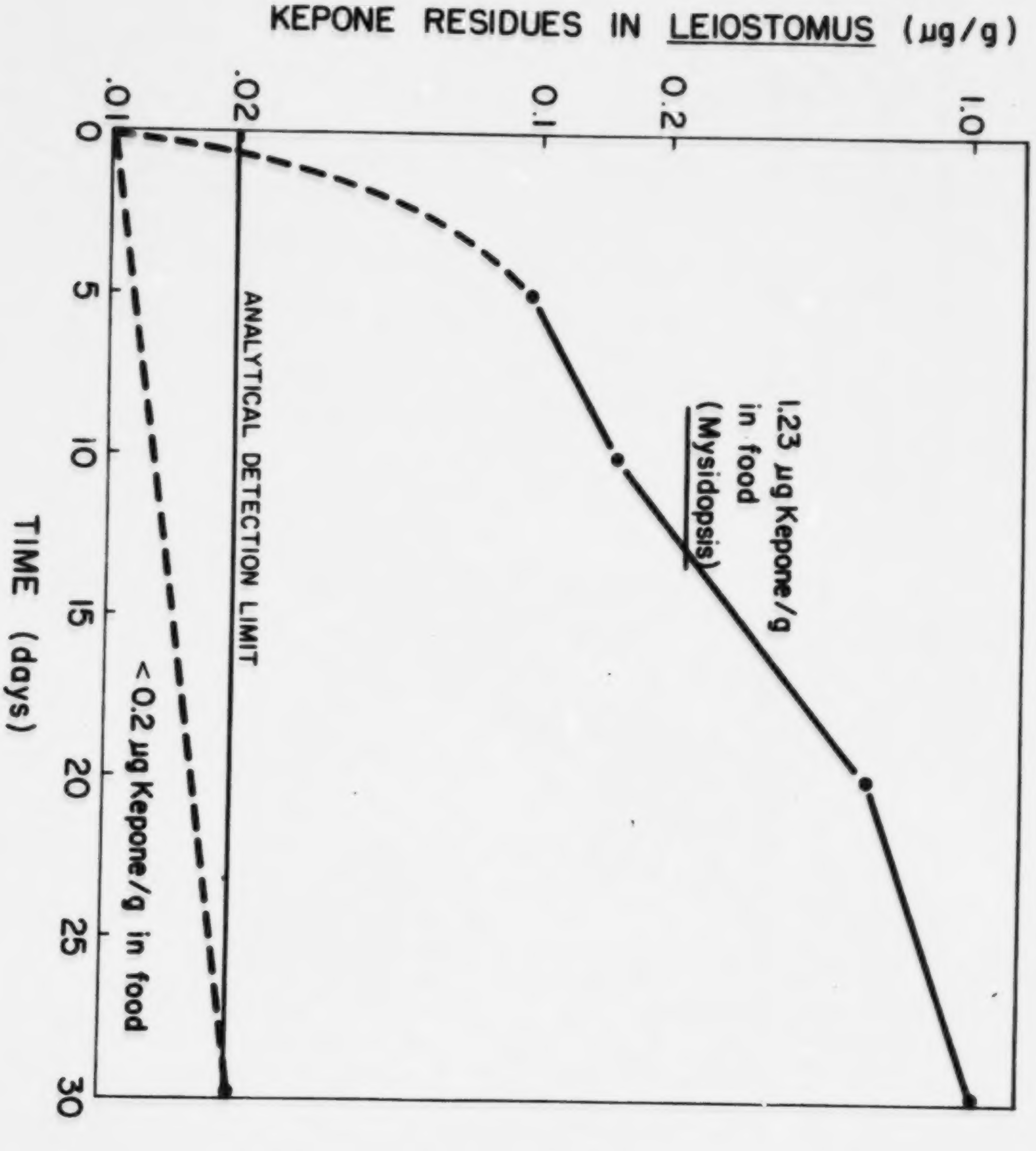

KEPONE RESIDUES IN LEIOSTOMUS (µg/g)
1.0
0.2
0.1
.02
.01
0
5
10
15
20
25
30
TIME (days)
1.23 µg Kepone/g in food (Mysidopsis)
ANALYTICAL DETECTION LIMIT
< 0.2 µg Kepone/g in food

Fig. 7. Bioaccumulation of Kepone by oysters (Crassostrea virginica) that consumed algae (Chlorococcum sp.) with residues of 34 µg Kepone/g (wet weight). Oysters fed on contaminated algae for 14 days (mean water temperature 22°C; mean salinity 19 °/oo), and were then fed uncontaminated plankton for an additional 10 days to allow depuration of the chemical. ND = not detectable, <0.02 µg/g wet weight.

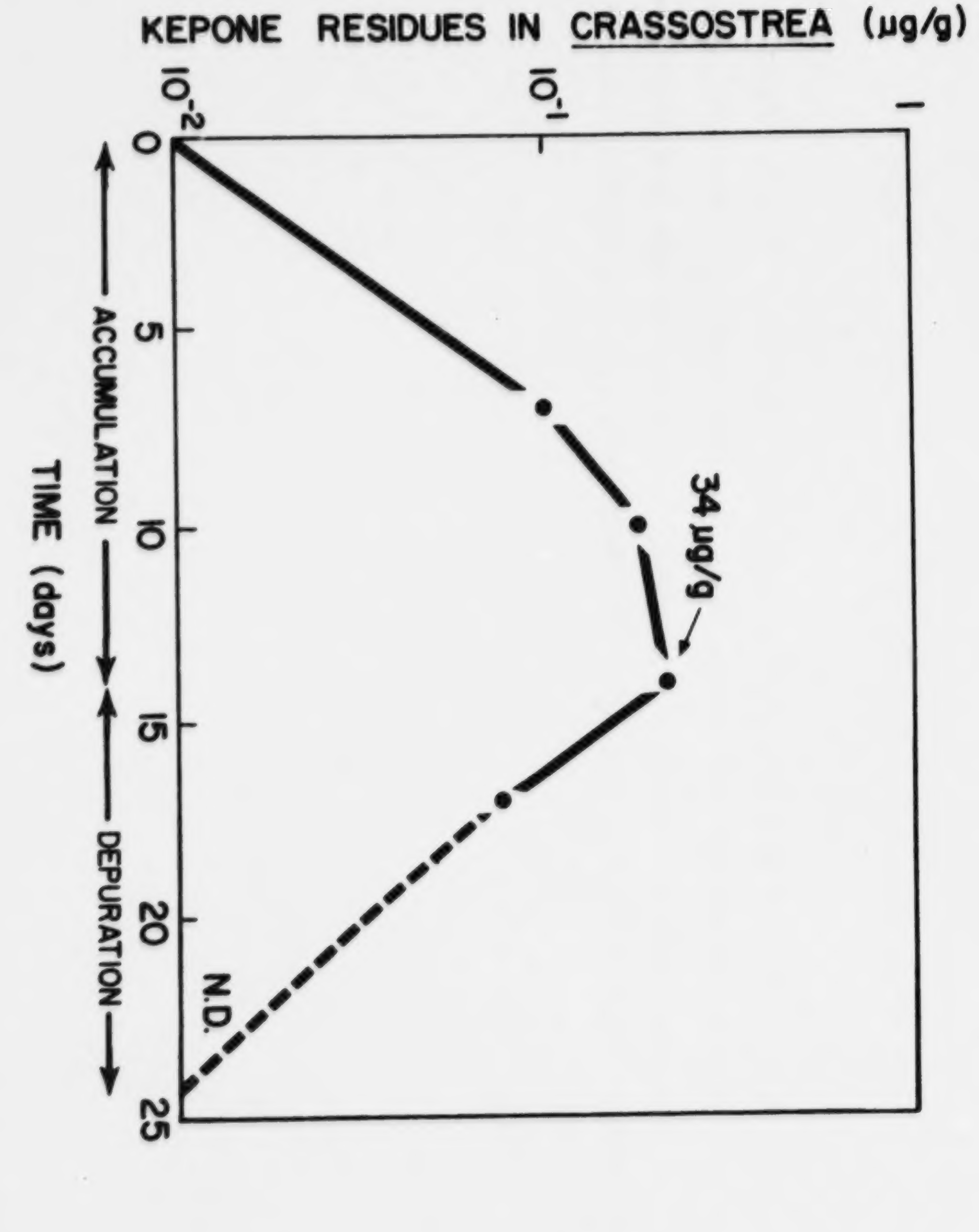
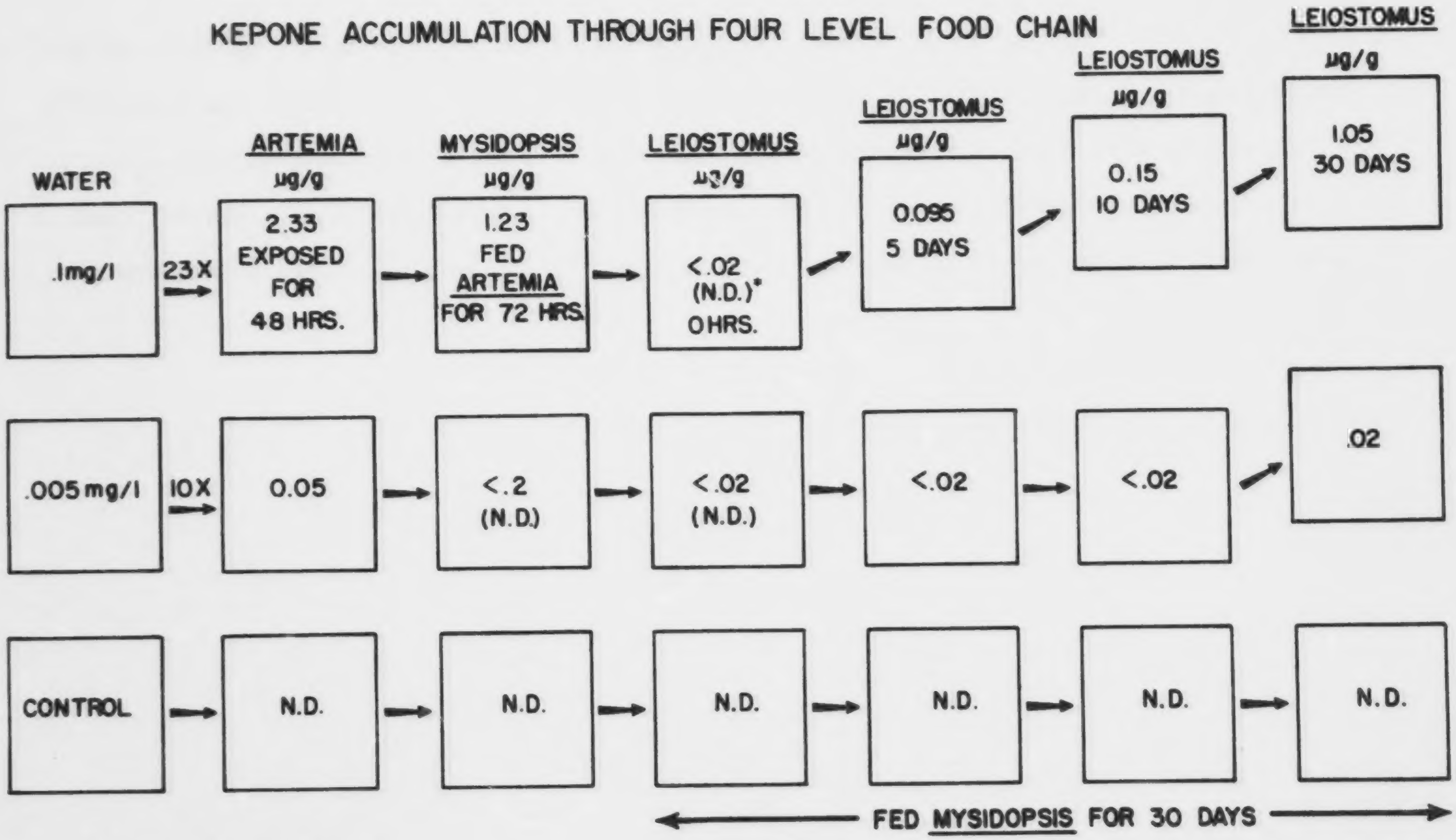

KEPONE RESIDUES IN CRASSOSTREA (µg/g)
10⁻²
10⁻¹
1
0
5
10
15
20
25
34 µg/g
N.D.
ACCUMULATION
DEPURATION
TIME (days)

Fig. 8. Block diagram of four-level food chain. Nominal concentrations of Kepone in water (left) were control (bottom), 0.005 mg/ℓ (center), and .1 mg/ℓ (top). Artemia salina nauplii, hatched in these concentrations of Kepone, were fed to mysids (Mysidopsis bahia), and mysids were fed to spot (Leiostomus xanthurus) for 30 days. Average measured concentrations of Kepone in each trophic species is given. Mean water temperature was 19°C and mean salinity 18 ^{o}/oo.

KEPONE ACCUMULATION THROUGH FOUR LEVEL FOOD CHAIN


WATER
.Img/I
23X
ARTEMIA
µg/g
2.33
EXPOSED
FOR
48 HRS.
MYSIDOPSIS
µg/g
1.23
FED
ARTEMIA
FOR 72 HRS.
LEIOSTOMUS
µg/g
<.02
(N.D.)*
0 HRS.
LEIOSTOMUS
µg/g
0.095
5 DAYS
LEIOSTOMUS
µg/g
0.15
10 DAYS
LEIOSTOMUS
µg/g
1.05
30 DAYS
.005 mg/I
10X
0.05
<.2
(N.D.)
<.02
(N.D.)
<.02
<.02
.02
CONTROL
N.D.
N.D.
N.D.
N.D.
N.D.
N.D.
FED MYSIDOPSIS FOR 30 DAYS

* N.D. = NON-DETECTABLE

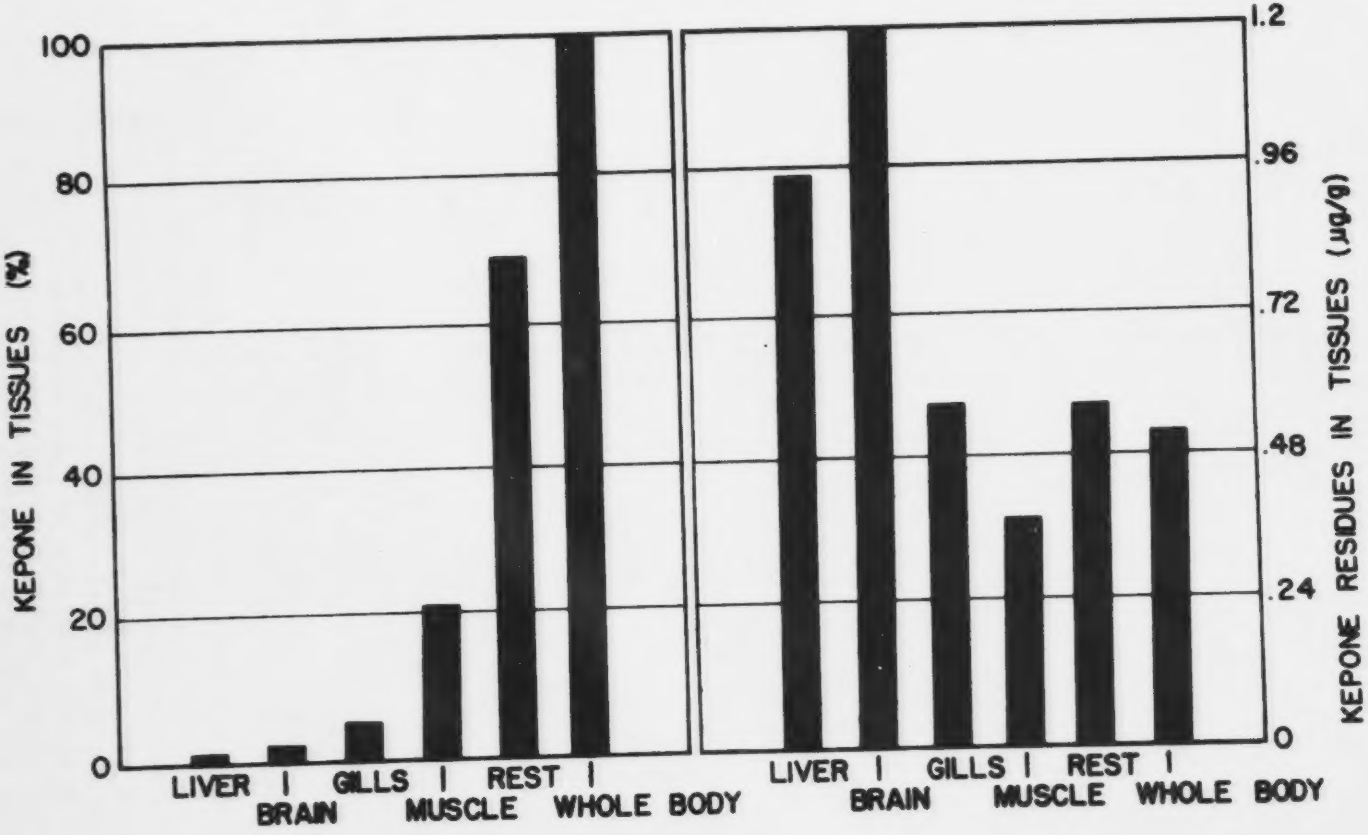


Fig. 9. Bioaccumulation of Kepone by spot (Leiostomus xanthurus) fed contaminated mysids (Mysidopsis bahia) containing average measured whole-body residues of <.2 (0.023 estimated) or 1.23 µg Kepone/g wet tissue. Detection limit for Kepone in spot tissues was ≥0.02 µg/g. Mean water temperature was 19°C and mean salinity 18 °/oo.

TABLE 1. Concentrations of Kepone (µg/g wet tissue) measured in oysters (*C. virginica*) exposed to 0.03 or 0.39 µg/ℓ for 28 days, mysids (*M. bahia*) exposed to 0.026 or 0.43 µg/ℓ for 21 days, grass shrimp (*P. pugio*) exposed to 0.023 or 0.40 µg/ℓ for 28 days, sheepshead minnows (*C. variegatus*) exposed to 0.05 µg/ℓ for 28 days, and spot (*L. xanthurus*) exposed to 0.029 or 0.4 µg/ℓ for 30 days in flowing water experiments. Animals were allowed to depurate Kepone for up to 28 days in Kepone-free flowing seawater.

Duration of Exposure (Days)	Oysters 0.03 µg/ℓ Whole Body	Oysters 0.39 µg/ℓ Whole Body	Mysids 0.026 µg/ℓ Whole Body	Mysids 0.43 µg/ℓ Whole Body	Shrimp 0.023 µg/ℓ Whole Body	Shrimp 0.40 µg/ℓ Whole Body
1/6	0.012	0.19				
1/3	0.031	0.53				
1	0.036	0.96	–	–	–	–
2	–	–	–	–	<0.02	0.27
3	–	–	–	–	–	–
4	0.11	1.3	<0.04	<0.04		
7	–	–	0.16	0.33	0.038	0.47
8	0.18	2.2				
9	–	–	–	–	0.072	1.79
11	–	–	0.15	6.3		
12	0.21	2.4				
14	–	–	0.19	4.7	0.088	2.18
15	0.20	2.5	–	–	–	–
19	0.29	3.5				
21	0.23	3.6	0.12*	4.8*	0.12	3.15
25	0.19	2.7				
28	0.21*	2.2*	–	–	0.087*	4.57*
30	–	–	–	–	–	–
Duration of Depuration						
1/6	0.30	2.1				
1/3	0.30	2.7				
1	0.14	1.4				
2	–	–	–	–	0.1	2.62
4	0.074	0.18				
7	<0.01	0.18	–	–	0.1	2.5
11	<0.01	0.055				
14	<0.01	0.039	–	–	0.084	1.78
21	<0.01	0.039	–	–	0.055	1.5
24	–	–	–	–	–	–
28	<0.01	< 0.01	–	–	0.035	0.84

*Final day of exposure.

TABLE 1. (continued).

Duration of Exposure (Days)	Minnows 0.05 µg/ℓ Muscle	Minnows 0.05 µg/ℓ Whole Body	Spot 0.029 µg/ℓ Muscle	Spot 0.029 µg/ℓ Whole Body	Spot 0.40 µg/ℓ Muscle	Spot 0.40 µg/ℓ Whole Body
1/6						
1/3						
1	<0.01	<0.01				
2						
3	0.019	0.031				
4						
7	0.086	0.14	<0.02	0.037	0.50	0.73
8						
9						
11						
12						
14	0.19	0.22				
15	-	-	0.055	0.072	0.86	0.76
19						
21	0.21	0.24				
25						
28	0.29*	0.37*				
30	-	-	0.048*	0.093*	0.99*	0.94*
Duration of Depuration						
1/6						
1/3						
1						
2						
4						
7	0.21	0.22	0.074	0.093	0.87	1.04
11						
14	-	-	-	-	0.57	0.72
21						
24	-	-	0.031	0.0469	0.38	0.52
28						

*Final day of exposure.

TABLE 2. Bioconcentration factors for selected species exposed to measured concentrations of Kepone in water.

Species	Exposure Concentration (μg/ℓ)		Duration of Exposure (days)	Mean Bioconcentration Factor
Chlorococcum sp.	100.	(static)	1	340
Crassostrea virginica	0.03		19	9,354
"	0.39		21	9,278
Artemia salina	5.	(static)	2	10
"	100.	(static)	"	23
Mysidopsis bahia	0.026		21	5,962
"	0.41		"	13,473
Palaemonetes pugio	0.023		28	5,127
"	0.4		"	11,425
Cyprinodon variegatus	0.05		"	7,115
Leiostomus xanthurus	0.029		30	3,217
"	0.4		"	2,340
"	1.5*		4	1,120
"	3.4*		"	941
"	4.4*		"	1,591
"	12.0*		"	900
"	16.0*		"	1,050

*Data from Schimmel and Wilson (in press).

TABLE 3. Concentrations of Kepone (µg/g whole body, wet tissue) measured in oysters (*C. virginica*) fed algae (*Chlorococcum* sp.) containing 34 µg/g for 14 days and in spot (*L. xanthurus*) fed mysids (*M. bahia*) containing 0.02 µg/g (estimated) or 1.03 µg/g for 30 days in flowing water experiments. Oysters were fed uncontaminated plankton for an additional 10 days to allow depuration of the chemical.

Duration of Exposure (Days)	Oysters fed 34 µg/g	Spot fed 0.02 µg/g (Estimated)	Spot fed 1.03 µg/g
	µg/g Whole Body	µg/g Whole Body	µg/g Whole Body
0	<0.02	<0.02	<0.02
5	-	<0.02	0.095
7	0.10	-	-
10	0.18	<0.02	0.15
14	0.21*	-	-
20	-	<0.02	0.59
30	-	0.015,0.024*	1.0,1.1*
Duration of Depuration			
3	0.075	-	-
10	<0.02	-	-

*Final day of exposure.

TABLE 4. Kepone transfer in algae-oyster food chain. Algae (*Chlorococcum* sp.) grown in Kepone enriched media for 24 hrs was fed to oysters (*C. virginica*) for 14 days in flow-through feeding experiment.

	Control food chain	Exposed food chain
(1) Kepone (single dose) in algal media (mg/ℓ)	Control	0.1
(2) Kepone residues in algae after 24 hrs of exposure (mg/kg)	Control (ND)*	$\overline{X} = 34$
(3) Bioconcentration factor from water [(2)/(1)]	--	340
(4) Kepone residues in oysters after 14 days of feeding	Control (ND)	0.21
(5) Bioaccumulation factor from algae to oysters [(4)/(2)]	--	.007
(6) Food chain factor [(4)/(1)]	--	2.1

*ND = non-detectable (<0.02 mg/kg).

TABLE 5. Kepone transfer in plankton-mysid-fish food chain. Brine shrimp (*A. salina*) were hatched during 48 hrs in Kepone enriched seawater and were fed to mysids (*M. bahia*) for 72 hrs. Mysids were then fed to spot (*L. xanthurus*) for 30 days in flow-through feeding experiment.

	Control food chain	Low Exposure food chain	High Exposure food chain
(1) Kepone (single dose) in brine shrimp media (mg/ℓ)	Control	0.005	0.1
(2) Kepone residues in brine shrimp after 48 hrs of exposure (mg/kg)	Control (ND)*	0.049 0.043 0.058 $\bar{x}$ = 0.050	1.3 2.4 3.3 $\bar{x}$ = 2.33
(3) Bioconcentration factor from water [(2)/(1)]	--	10.	23.3
(4) Kepone residues in mysids after 72 hrs of feeding (mg/kg)	Control (ND)	$\bar{x}$ = 0.023 (estimated)	0.89 1.0 1.8 $\bar{x}$ = 1.23
(5) Bioaccumulation factor from brine shrimp to mysids [(4)/(2)]	--	0.5 (estimated)	0.53
(6) Kepone residues in spot after 30 days of feeding (mg/kg)	Control (ND)	0.015 0.024 $\bar{x}$ = 0.0195	1.0 1.1 $\bar{x}$ = 1.05
(7) Bioaccumulation factor from mysids to spot [(6)/(4)]	--	>0.85 (estimated)	>0.85
(8) Food chain factor [(6)/(1)]	--	>3.9	>10.5

*ND = non-detectable (<0.02 mg/kg).

THE FATE AND DEGRADATION OF 14C-KEPONE IN ESTUARINE MICROCOSMS

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Contribution number 351

ABSTRACT

The fate of 14C-Kepone was studied in static and continuous flow estuarine microcosms. Biotic and abiotic transformation and volatilization were not important processes in these studies. Kepone desorbed readily from salt marsh sediments and James River sediments. While this desorption was independent of environmental temperatures and salinity ranges, Kepone residues in sediment influenced concentrations in the water column. Radioactivity was not extractable from some James River sediments, using recognized analytical procedures. In larger continuous flow systems, benthic polychaetes (Arenicola cristata) accumulated high residues of Kepone, died, and decomposed. These residues were never available for desorption compared to sediment. These data will allow better prediction of the fate of Kepone in the aquatic environment.

INTRODUCTION

The Environmental Research Laboratory at Gulf Breeze provides EPA with data related to water quality criteria, pesticide registration, and ocean dumping. Following the contamination of the James River system with Kepone (Figure 1), our facility responded with necessary data about the toxicity of Kepone to estuarine organisms and its potential for bioaccumulation and biomagnification (Bourquin *et al*., 1977a; Hansen *et al*., 1977; Schimmel and Wilson, 1977; and Walsh *et al*., 1977). However, serious questions arose concerning the fate of Kepone in the river.

The fate of a pollutant is closely related to its toxicity; forces such as volatilization, sorption, metabolism, and abiotic transformation (photolysis, hydrolysis, chelation) affect the availability and toxicology of pollutants to aquatic species. A knowledge of the sites of Kepone concentration and rates of exchange associated with these sites is necessary for long term regulatory actions. Sorption and transformation data are needed to determine whether the ecosystem can remove the pollutant by degradation or eventual washout, or whether physical assistance from dredging or damming is necessary.

Presently, the research project at Manhatten College is directed towards the mathematical analysis and modeling of Kepone in the James River. The projection of time required to reduce the levels of Kepone by various natural processes such as adsorption-desorption and transformation are included as an important phase of the project. Unfortunately, insufficient data are available for Kepone.

A variety of laboratory microcosms have been developed to study the fate of pollutants in the estuarine environment (Bourquin *et al*., 1977b). In the following paper, two of these systems were used to examine the potential for movement and transformation of 14-C Kepone. These data complement other existing research efforts and allow better prediction of the environmental fate of Kepone with a minimum of assumptions.

MATERIALS AND METHODS

Sediment Collection and Characterization

Range Point sediment was collected from a salt marsh located on Santa Rosa Sound near Gulf Breeze, Florida. The sediment was passed through a 2mm stainless steel sieve and fractionated into water-suspendable particulate (P) and heavier sediments (S). The suspendable particulate was primarily organic detrital material and combusted completely following ignition. The heavier sediments were mainly quartz sand with little organic content.

Sediment grab samples were collected on two separate occasions from the James River system. The first samples (4/26/77) were obtained from the estuary and stored at Gulf Breeze under flowing filtered seawater where they were used for the majority of the studies to be reported. The second set of samples (8/1/77) was collected from the river where the turbidity maximum had settled during the summer. Sediments were characterized (Table I) for total organic carbon on ignition (500°C, 4 hours) and for particle size using the settling rate--soil hydrometer method (ASTM method D422-63, 1964). While the first set of samples failed to yield any significant Kepone residues, the second set of samples contained 0.18 ppm Kepone (personal communication, A.J. Wilson, EPA, Gulf Breeze, Florida).

Since the majority of James sediment was clay-like material, Kaolinite and Bentonite clays (Ward Scientific) were included in these studies as reference sediments (Bailey and White, 1970).

Environmental Fate Screening System

A system (Figure 2) consisted of a 125 ml Erlenmeyer flask fitted with a No. 5 Neoprene stopper. A capillary glass gas inlet allowed introduction of air or nitrogen; the gas exit was fitted to a disposable Pastuer pipette filled with XAD-4 resin (Rohm and Haas, Philadelphia, Pa.) to trap volatile compounds. The small size of the system allowed maximum replication and examination of different environmental substrates and processes. Similar systems were sampled sequentially with time to indicate rates of transport and transformation.

14C-Kepone was used to minimize involved analysis and to facilitate simulation of environmental levels. This chemical was provided by Allied Chemical Corp. (Princeton, New Jersey) with a specific activity of 24.3 μCi/μM and a purity of 99%. A stock solution was prepared in acetone such that 10 μl was equivalent to 19.9 μg (1,941,000 dpm).

In the standard analytical procedure (Figure 3), the system was fractionated into water, suspendable particulate, and unsuspendable sediment or sand by repeated rinsing of the system with equivalent salinity water; James sediments were all suspendable with this procedure and were not fractionated any farther. Following centrifugation (3000 RPM), an aliquot of the water was examined for radioactivity by scintillation counting (Beckman LS-250 Liquid Scintillation System, Atlanta, Georgia). The sediment fractions were extracted repeatedly with acetonitrile, with aliquots taken for scintillation. Following the addition of 2% sodium sulfate water to the solvent extracts (4:1 water/solvent), the aqueous fractions were extracted with organic solvent (1:1 petroleum ether/diethyl ether) and analyzed by thin layer chromatography (3:1 diethyl ether/n-hexane; Quanta Gram LQCDF, Quanta Industries, Fairfield, New Jersey) and autoradiography (Birchover Radiochromatogram Spark Chamber, Hitchin, England). Periodically, the extracts were cleaned on florisil columns (2 gm, hexane washed; 20 ml rinse of 5% diethyl ether/hexane; final elution with 50 ml of 1% methanol/benzene) and analyzed for Kepone, octachloro-Kepone, and nonachloro-Kepone (standards provided by A. J. Wilson, EPA, Gulf Breeze, Florida) by electron capture gas chromatography (Hewlett-Packard GC Model 5830A; Ni^{63}detector; Model 18850A GC terminal; 2 mm id x 2 m glass, 2% OV-101 on Gas Chrom Q, 100/120). Extracted sediments were dried and combusted at 900°C (Harvey Instrument OX-200 Combustion System, Hillsdale, New Jersey) to liberate and trap residual radioactivity as $^{14}CO_2$.

The XAD-4 resin traps were eluted with 4 ml portions of acetonitrile directly into two scintillation vials. Since all routes of exit from the systems were sampled and all system components were subjected to a total analysis, a reliable budget for radioactivity recovery was calculated for quality control of the data.

Standard experimental conditions included 10 gm (wet weight) of sediment; 100 ml of Santa Rosa Sound water (18-24 ppth); constant temperature of 25°C; 12/12 hr. diurnal lighting (G.E. Vita Gro); water saturated air (Silent Giant); 19.9 μg 14-C-Kepone (1,941,000 dpm) added in 10 μl acetone carrier to water column after 48 hr. acclimation period; and duplicate systems sampled. As an indicator of desorption, water was periodically exchanged in systems halfway between sampling days by centrifugation of the system sediment and water (3000 RPM), decantation of water for analysis, and resuspension of sediment in fresh salt water.

For Range Point studies, 50 gms (wet weight) of unsuspendable sediment and 2 gms (wet weight) of suspendable sediment were added to each system.

Systems were sterilized by addition of 2 ml (2% v/v) Formalin. Throughout the study, sterility was confirmed by plating 0.1 ml samples of water on Zoebell's media (15 ppth) and observing the lack of colony formation.

Anaerobic systems were completely stoppered throughout the study and were periodically purged with nitrogen gas.

For salinity studies, low salinity water (0-3 ppth) was collected from the Lower Escambia River and high salinity water (28-35 ppth) was collected from the Gulf of Mexico. James sediment remained suspended in low salinity systems; radioactivity in water was measured after normal centrifugation (Wpre; 3000 RPM) and again after higher centrifugation (Wpost; 10,000 RPM).

Outdoor studies (June, 1977) were conducted at Sabine Island (Gulf Breeze, Florida); sunlight effects were examined by comparing light exposed systems to dark controls (foil-covered). Temperature in the flasks fluctuated from 15°C to 45°C.

The effect of Kepone concentration was studied by either amending the isotope with unlabeled Kepone (Chem Service, Inc.) to produce a tenfold higher concentration than normal (200 μg/system) or diluting to provide a tenfold lower concentration (2 μg/system).

For Kaolinite and Bentonite clay studies, 10 gm (dry weight) of clay and 100 ml of Santa Rosa Sound water were used. Higher centrifugation speeds (10,000 RPM) were required to separate the sediment from the water.

Continuous Flow System

These systems were designed to study the fate of pollutants resulting from the biological activity of aquatic macro biota. A system (Figure 4) consisted of a standard 38 liter glass aquarium fitted with a plexiglass lid containing sampling portals. Air and water entered and exited the system through glass tubing coupled to No. 8 Neoprene stoppers. Raw filtered sea water (18-24 ppth) was continuously fed through the system with a Harvard Model 1203 peristaltic pump. The system was aerated continuously, with exiting air sampled for volatiles by XAD-4 resin traps.

For these studies two systems were structured with 9 cm of Range Point sediment and Santa Rosa Sound water to the 28 liter mark. The systems were allowed to acclimate static with aeration for 48 hrs. (25°C; 12/12 diurnal lighting). Twelve lugworms (Arenicola cristata) were added to one of the tanks and a flow rate of 1 ℓ/hr was started through both systems (washout rate = 0.1 hr^{-1}); after four days, the water flow was stopped and each system was spiked with 1 mg (100×10^6 dpm) of 14C-Kepone in 0.5 ml acetone. After two days the water flow was again started at 1 ℓ/hr for both systems. Aliquots of water (3 ml) were sampled directly for radioactivity until background levels were obtained.

Two beds of XAD-4 resin (75 ml wet volume in 250 ml separatory funnel) were alternated at the water exit of each system every 48 hr; following removal from a system, the resin was transferred to a glass thimble and extracted with methanol in a Soxhlet extractor overnight. Following extraction the resin was returned to the separatory funnel, rinsed with water, and used again. Aliquots of the methanol were analyzed directly for radioactivity; like the analytical procedure with the screening systems, the methanol was diluted with 2% sodium sulfate water, extracted, and analyzed by thin layer chromatography/autoradiography and gas chromatography. Cores were obtained by inserting a 1.5 cm i.d. teflon tube into the sediment column, sealing the top of the tube with a Neoprene stopper, and extruding the intact core. Cores were fractionated and analyzed like the screening systems.

Lugworms and algae were homogenized with acetonitrile; the solvent was diluted with aqueous sodium sulfate and extracted and analyzed like the screening systems.

RESULTS

Environmental Fate Screening System

Initial studies examined Kepone fate with reference sediments. Previous experience with salt marsh sediment from Range Point (Bourquin et al., 1977c), made it a good candidate for these studies; in addition, its high organic content represented one extreme situation environmentally. The results (Table II) with both unsterile and sterile (2% Formalin) systems demonstrate rapid movement of Kepone into the suspendable sediment extract fraction (Pe), with low levels present in the heavier sediments (Se). Volatility (R) and binding to sediment (Pc, Sc) were not major mechanisms of Kepone transport in these sytems. Following the initial spike at Day 0, an equilibrium was established between the sediments and water. Constant levels of Kepone were maintained in the water column (W) even after system washing began on Day 13, resulting in a continuous removal of compound from the system. Sterility did not affect the movement of Kepone in these systems. Analysis of radioactivity failed to show any transformation of Kepone throughout the study.

Other reference sediments included Kaolinite (low surface area, low cation exchange capacity) and Bentonite (high surface area, high cation exchange capacity) clays. The results in Table III demonstrate differences in Kepone movement with these sediments. Both systems maintained higher Kepone levels in the water column compared to the Range Point systems, although the Bentonite systems more closely mimicked the salt marsh systems. Again binding and volatility were not significant in Kepone transport; however, greater levels were washed out of both clay systems with time compared to Range Point systems. Kaolinite studies displayed the greatest washout rate of any system studied with 65% removed from the system after three washings. Kepone did not decompose during these studies.

As was previously mentioned, grab samples were collected from the James River system on two separate occasions and displayed different particle size distributions and residues of Kepone. Experimental results with these sediments are found in Tables IV and V, comparing the effects of sterility and aerobiosis. The data indicate that in most cases the systems behaved similar to the Range Point studies. Aerobiosis and sterility did not affect movement of 14-C Kepone; again, degradation was lacking in all systems. However, it is worth noting the greater levels of bound radioactivity (Pc) in James sediments collected where the turbidity maximum had settled. This phenomenon was not observed with sediments collected earlier in the estuary or with Range Point sediments.

The remainder of these studies were conducted with James sediment collected from the estuary (4/26/77). Systems fortified with tenfold higher and tenfold lower concentrations of Kepone (Table VI) displayed radioactivity distribution similar to other studies mentioned. Again, Kepone did not degrade in these systems.

In studies with low salinity water, sediment remained suspended throughout the water column. Finer particles containing about ten percent of the total Kepone were not fractionated from these systems at standard centrifugate speeds; a higher degree of centrifugation resulted in Kepone water levels similar to high salinity systems and the previous studies mentioned. The suspension of sediment and salinity differences did not affect Kepone removal from the systems with the washing procedure; Kepone did not degrade during this study.

The data in Table VIII reflect the effects of environmental sunlight and temperature on Kepone movement and transformation. Comparison of these data with other systems demonstrate little difference in radioactivity distribution or washout. Kepone did not degrade in these studies after 42 days of outdoor exposure.

Continuous Flow System

With the water flow conditions of this experiment (1 ℓ/hr, 48-72 hrs/resin bed), the resin was efficient in the removal of ^{14}C-Kepone from raw seawater (>99%); the Soxhlet extraction procedure removed all radioactivity from the resin throughout these studies (>95% recovery). Table IX contains the levels of radioactivity found in aliquots of water from each system for the first two weeks of the study. Radioactivity disappeared faster from water in the system containing lugworms, with only half as much as the system without lugworms by Day 2 when the flow was started. At that time some of the lugworms moved to the surface of the sediment, an indication of unfavorable conditions; by Day 5 all of the lugworms were dead, with fungal mats forming over the tissues. One lugworm was removed from the system and found to contain high levels of radioactivity in its tissues (3% of total spike to system); all of the radioactivity was Kepone. At these levels of accumulation, the biological component added to this system could contain a large fraction of the original fortification (3% x 12 = 36%) and would account for the more rapid removal of radioactivity from the water in that system. The other dead lugworms were left in the system, where they eventually decayed and completely decomposed.

The radioactivity collected from the beds of resin at the water exit was graphed over time as DPM/24ℓ to compensate for irregularities in sampling periods. The data in Figure 5 indicate a similar washout rate of radioactivity from both systems over the first 70 day period. By Day 48, eighty percent of the original fortification had washed out of the system without lugworms and only 40% had exited the lugworm system. All of this radioactivity was analyzed as Kepone. By that time the lugworms were completely decomposed and fungal colonies had disappeared from the sediment surface; however, the radioactive Kepone present in the tissues was not as available for washout as that present in the sediment.

In fact for the following 42 days (Figure 6), only 4% more Kepone was washed out from each system. During that time the water flow rate affected the condition of the systems and export of Kepone. At a flow rate of 0.5 ℓ/hr, large mats of algae began to grow on the glass walls and sediment surface; and Kepone levels in exiting water equilibrated at 60 pptr. Samples of the algae never contained appreciable levels of radioactivity. At a flow rate of 0.75 ℓ/hr, the algae disappeared from the glass walls and sediment surface; and Kepone residues in water reached a new equilibrium at 40 pptr.

Cores taken throughout the study showed 14C-Kepone present in the suspendable sediment fraction, with little indication of high levels of binding. Cores from the lugworm system taken later in the study (after Day 60), contained 30-40% higher levels of radioactivity compared to the system without lugworms. Analysis again revealed only Kepone present in the radioactivity.

DISCUSSION

These systems were used to indicate the major environmental components affecting the fate of Kepone. Extrapolation of these data to the James River system is hampered by severe scaling problems and inadequacies in the experimental protocol. However, these studies do validate current field monitoring practices and offer direction for future field work to supplement the existing data base for mathematical modeling.

Volatilization and transformation were not significant processes affecting Kepone in these studies, which implies that they may not be important mechanisms of Kepone removal from the James River. Concern with the possible environmental formation of dechlorinated products of Kepone and their accumulation in tissues and sediment may be unwarranted; Kepone contaminating the James River is confined to the aquatic component and does not represent a hazard to surrounding terrestrial communities from air transport. Current monitoring programs need not expand analytically to include these two areas of potential Kepone fate.

The failure to extract radioactivity from sediment has been characterized as an indication of bound residues. The significance of bound residues relative to their environmental dissipation, monitoring, and toxicology has been addressed by others (Kaufman et al., 1976). The availability of these residues for export or accumulation is an area that requires further investigation. In these studies bound residues were only associated with sediments collected from the turbidity maximum, which already contained high levels of Kepone and a greater proportion of small particle sizes. The immediate question relative to the James River system is whether binding to sediments occurs to any great extent or is merely an isolated event. Further studies with these systems using other sediments from the James River could answer this question. Kepone levels in sediments from field studies may be only conservative figures.

Studies with different concentrations of Kepone, water salinity, and system temperature did not show any changes in the relative percent distribution or washout of Kepone. Kepone levels in the water were independent of temperature and salinity, although lower salinity enhanced suspension of sediments containing Kepone. However, Kepone concentrations in the water column were proportional to the concentrations in the sediment. Systems at the high concentration (200 µg) contained 100 times the water and sediment radioactivity of the low concentration systems at any time; Kepone levels washed out of the high concentration systems were 100 times those of the low concentration systems. During washout, as Kepone levels in sediments decreased, concentrations in the water column decreased. While Kepone levels collected in the water resin beds of the continuous flow systems equilibrated with time, the overall trend was decreasing Kepone concentrations in the water that correlated with lower residues in the sediments. Environmentally, higher concentrations of Kepone detected in water may be indicative of higher Kepone residues in sediments.

Washout of radioactivity from all systems correlated with decreasing levels of Kepone in sediment extracts. Except for Kaolinite clay studies, the type of sediment did not affect the desorption of Kepone. The Kepone equilibrium between sediment and water was not biologically mediated. The potential for Kepone movement from sediment is important environmentally and represents a continuous source of exposure to aquatic organisms. In addition, this process is a mechanism of Kepone removal from the James River system. Greater emphasis on water monitoring programs using high volume sampling methods will provide data related to Kepone concentrations in sediments and Kepone export from the system. However, the recalcitrant nature of Kepone, together with its dynamic movement potential, forecast an environmental impact reaching beyond the James River system.

Lugworms in continuous flow systems accumulated high levels of Kepone; Kepone did not desorb from these tissues following their decomposition, although it was solvent extractable. Kepone has a stronger association with biological tissue compared to sediment; this phenomenon could influence the distribution of Kepone in the James River and may account for the correlation of high sediment organic content with corresponding high residues of Kepone from monitoring efforts (personal communication, Robert Huggett, Virginia Institute of Marine Science).

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TABLE I

SEDIMENT CHARACTERIZATION[4]

	I[1]	I	II[2]		
	4/26/77	6/15/77	8/1/77	Kaolinite	Bentonite
Total Organic on Ignition[3]	1.4%	1.5%	4.4%	4.1%	0.01%
Sand (2.0 - 0.5 mm)	47.4%	44.3%	9.4%	8.8%	6.0%
Old Silt (0.05 - 0.005 mm)	20.2%	25.5%	29.1%	25.1%	5.2%
New Silt (0.05 - 0.002 mm)	20.2%	27.5%	34.5%	34.1%	6.2%
Old Conventional Clay (<0.005 mm)	32.4%	30.2%	61.5%	66.1%	88.8%
New Conventional Clay (<0.002 mm)	32.4%	28.2%	56.1%	57.1%	87.8%

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[1] James Sediment I: Collected 4/26/77; used up to 6/15/77 for all studies;

[2] James Sediment II: Collected 8/1/77

[3] 500°C; 4 hours.

[4] ASTM method D422-63, 1964. Settling rate-soil hydrometer method.

TABLE II

RANGE POINT SYSTEMS - STERILE AND UNSTERILE

DAY	W	Se	Sc	Pe	Pc	R	WASH	TOTAL
Unsterile								
0	12.0	1.9	0.1	78.7	2.1	--	--	94.8
3	5.4	4.0	0.5	69.8	4.2	0.2	--	84.1
6	5.8	3.5	0.7	75.5	6.2	0.1	--	91.8
10	5.6	4.0	0.8	61.8	4.3	0.1	--	76.6
13	5.2	3.8	1.0	69.6	6.4	0.2	--	86.2
17	3.8	5.8	1.2	67.4	5.5	0.2	4.6	88.5
24	4.0	6.2	1.2	60.1	5.5	0.2	7.9	85.1
31	3.6	5.4	1.0	43.7	4.7	0.1	11.8	70.3
Sterile								
0	13.6	4.5	0.2	74.4	1.4	--	--	94.1
1	9.4	4.1	0.1	76.7	1.9	0.1	--	92.3
3	6.7	1.8	0.1	79.0	2.6	0.1	--	90.3
6	7.3	1.9	0.2	73.9	3.5	1.3	--	88.1
10	6.9	2.6	0.3	72.0	4.1	0.5	--	86.4
13	6.9	2.3	0.4	69.5	5.6	0.5	--	85.2
17	3.6	5.7	0.9	64.4	3.5	1.4	7.1	86.6
24	3.3	7.2	1.2	55.3	4.0	0.7	10.4	82.1
31	3.1	7.3	1.2	41.1	4.2	1.0	14.4	72.3

TABLE III

KAOLINITE AND BENTONITE SYSTEMS

DAY	W	Pc	Pc	R	WASH	TOTAL
Kaolinite						
0	48.3	53.1	1.5	--	--	102.9
8	39.3	52.2	1.1	0.4	--	93.0
15	35.0	50.2	2.0	2.0	--	89.2
28	14.4	34.0	1.7	5.1	29.8	65.0
35	10.0	17.4	2.8	7.8	48.7	86.7
42	7.4	15.7	7.0	1.1	65.8	97.0
Bentonite						
0	70.7	27.8	2.6	--	--	101.1
8	26.7	55.8	3.2	2.6	--	88.3
15	16.6	58.0	3.6	3.0	--	81.2
28	7.3	54.6	5.0	7.3	15.6	89.8
35	6.8	53.4	5.0	5.3	24.1	94.6
42	6.1	48.9	6.4	2.5	32.3	96.2
49	3.9	36.7	9.9	2.6	39.0	92.1

TABLE IV

JAMES RIVER SYSTEMS - AEROBIOSIS AND STERILITY

DAY	W	Pe	Pc	R	WASH	TOTAL
Unsterile - Aerobic						
0	18.5	76.9	2.1	--	--	97.5
11	13.0	74.0	5.8	0.3	--	93.3
18	6.1	58.4	2.2	0.4	9.7	76.8
25	4.5	41.8	3.8	0.1	12.5	62.7
Sterile - Aerobic						
0	16.2	74.5	2.1	--	--	92.8
11	12.3	74.6	5.0	0.4	--	92.3
18	6.4	61.2	1.7	0.2	11.4	80.9
25	3.7	41.6	3.1	1.7	14.1	64.2
Unsterile - Anaerobic						
5	16.2	72.6	4.4	--	--	93.2
12	12.6	75.9	4.7	--	--	93.2
19	12.1	77.1	5.2	--	--	94.4
Sterile - Anaerobic						
5	18.8	72.5	2.7	--	--	94.0
12	13.4	74.7	1.8	--	--	89.9
19	11.2	76.6	6.7	--	--	94.5

TABLE V

JAMES RIVER SYSTEMS II - COLLECTED 8/1/77; AEROBIOSIS

DAY	W	Pe	Pc	R	WASH	TOTAL
Aerobic						
0	15.9	76.8	5.4	--	--	98.1
7	8.1	68.7	26.2	0.1	--	103.1
14	7.2	68.2	23.7	0.2	--	99.3
25	3.9	77.3	10.4	0.2	5.3	97.1
32	3.3	54.0	21.4	0.1	10.5	89.3
40	3.2	42.8	36.0	0.2	13.7	95.9
47	3.0	53.9	20.4	0.5	17.7	95.5
Anaerobic						
0	12.1	68.3	16.7	--	--	97.1
7	6.3	74.3	18.3	--	--	98.9
14	8.2	72.1	18.1	--	--	98.4
25	5.6	79.3	7.8	--	6.5	99.2
32	4.1	53.5	30.7	--	12.6	100.9
40	3.4	41.1	36.6	--	15.6	96.7
47	3.3	48.0	22.8	--	20.5	94.6

TABLE VI

JAMES RIVER SYSTEMS - CONCENTRATION

DAY	W	Pe	Pc	R	WASH	TOTAL
Low Concentration						
0	20.4	72.0	6.1	--	--	98.5
7	13.2	75.4	7.3	0.4	--	96.3
14	11.9	70.7	6.5	0.5	--	89.6
24	7.4	70.1	6.6	0.6	12.4	97.1
30	6.6	55.2	7.1	1.1	18.9	88.9
35	6.1	64.0	7.4	1.3	26.0	104.8
42	6.3	55.8	6.6	1.2	32.8	102.7
High Concentration						
0	16.1	79.7	4.8	--	--	100.6
7	17.8	75.3	5.4	0.2	--	98.7
14	15.5	67.8	3.7	0.3	--	87.3
24	10.0	54.7	5.0	0.7	16.5	86.9
30	8.5	55.5	5.5	1.4	25.9	96.8
35	7.5	49.9	5.8	1.0	36.4	100.6
42	7.1	40.3	4.7	1.5	41.3	94.9

TABLE VII

JAMES RIVER SYSTEMS - SALINITY

DAY	Wpre	Wpost	Pe	Pc	R	WASH	TOTAL
Low Salinity							
0	36.8	--	55.6	2.4	--	--	94.8
3	27.1	18.9	65.0	4.3	0.1	--	96.5
6	25.9	16.8	59.7	4.6	0.2	--	90.4
10	20.8	14.7	71.9	4.7	0.4	--	97.8
14	22.2	13.4	67.1	5.4	0.8	--	95.5
18	11.6	7.8	64.9	5.8	0.3	12.8	95.4
25	8.7	5.9	59.8	5.5	0.4	19.4	93.8
32	6.4	5.2	55.7	4.9	0.5	24.1	91.6
39	6.4	4.6	52.5	5.6	0.3	30.5	95.3
High Salinity							
0	19.1	--	73.2	3.0	--	--	95.3
3	14.0	12.7	75.6	6.1	0.4	--	96.1
6	12.3	11.0	71.7	5.0	0.4	--	89.4
10	9.7	9.3	79.7	3.8	0.4	--	93.6
14	9.9	8.4	74.7	6.7	1.9	--	93.2
18	6.4	5.2	69.7	6.1	1.7	9.7	93.6
25	5.7	4.9	65.4	6.0	2.1	15.9	95.1
32	4.9	4.2	59.4	5.6	3.8	20.5	94.2
39	4.6	3.6	50.5	7.4	1.0	28.0	91.5

TABLE VIII

JAMES RIVER SYSTEMS - OUTDOOR STUDIES

DAY	W	Pe	Pc	R	WASH	TOTAL
Light						
0	18.4	69.4	3.1	--	--	90.9
3	19.2	69.4	4.8	0.4	--	93.8
7	16.3	69.7	5.4	1.0	--	92.4
10	14.7	67.7	7.6	0.9	--	90.9
13	11.6	71.4	7.5	0.6	--	91.1
23	9.4	59.1	9.3	1.5	12.7	92.0
32	9.6	45.0	6.5	1.2	24.3	86.6
36	7.1	33.8	4.7	5.1	31.3	82.0
42	5.1	33.3	5.0	2.6	38.6	84.6
Dark						
0	19.4	65.9	3.4	--	--	88.7
3	17.8	70.5	4.7	1.5	--	94.5
7	15.1	73.2	5.3	0.9	--	94.5
10	13.9	73.5	6.6	1.0	--	95.0
13	11.3	77.0	6.4	0.4	--	95.1
23	8.0	65.9	9.0	1.6	10.9	95.4
32	7.8	61.3	6.4	3.1	19.0	97.6
36	7.7	43.4	5.9	8.0	29.4	94.4
42	6.2	43.6	5.4	1.7	33.3	90.2

TABLE IX

RADIOACTIVITY IN WATER

Radioactivity DPM (3 ml Aliquots)

DAY	WITHOUT LUGWORMS	WITH LUGWORMS
0	16,720	16,320
1	10,790	6,650
2	8,650	4,640
2	begin flow - 1 ℓ/hr	
3	2,510	1,160
4	990	484
5	635	326
7	362	241
8	300	188
14	135	94

FIGURES

Figure 1. Kepone (decachlorooctahydro-1,3,4-metheno-2H-cyclobuta(cd) pentalene-2-one).

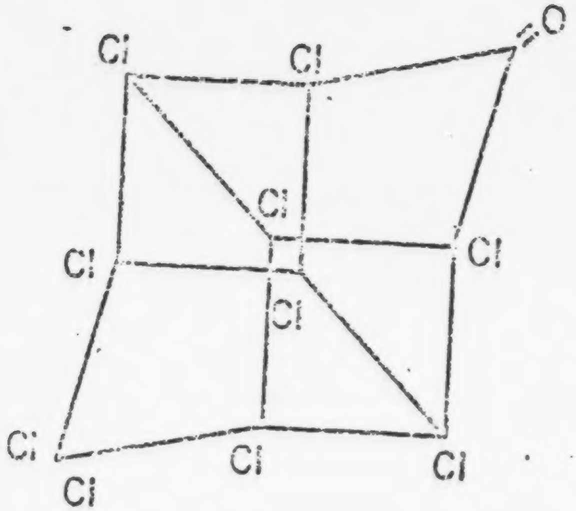
Figure 2. Environmental Fate Screening System.

Figure 3. Analytical Fractionation Procedure.

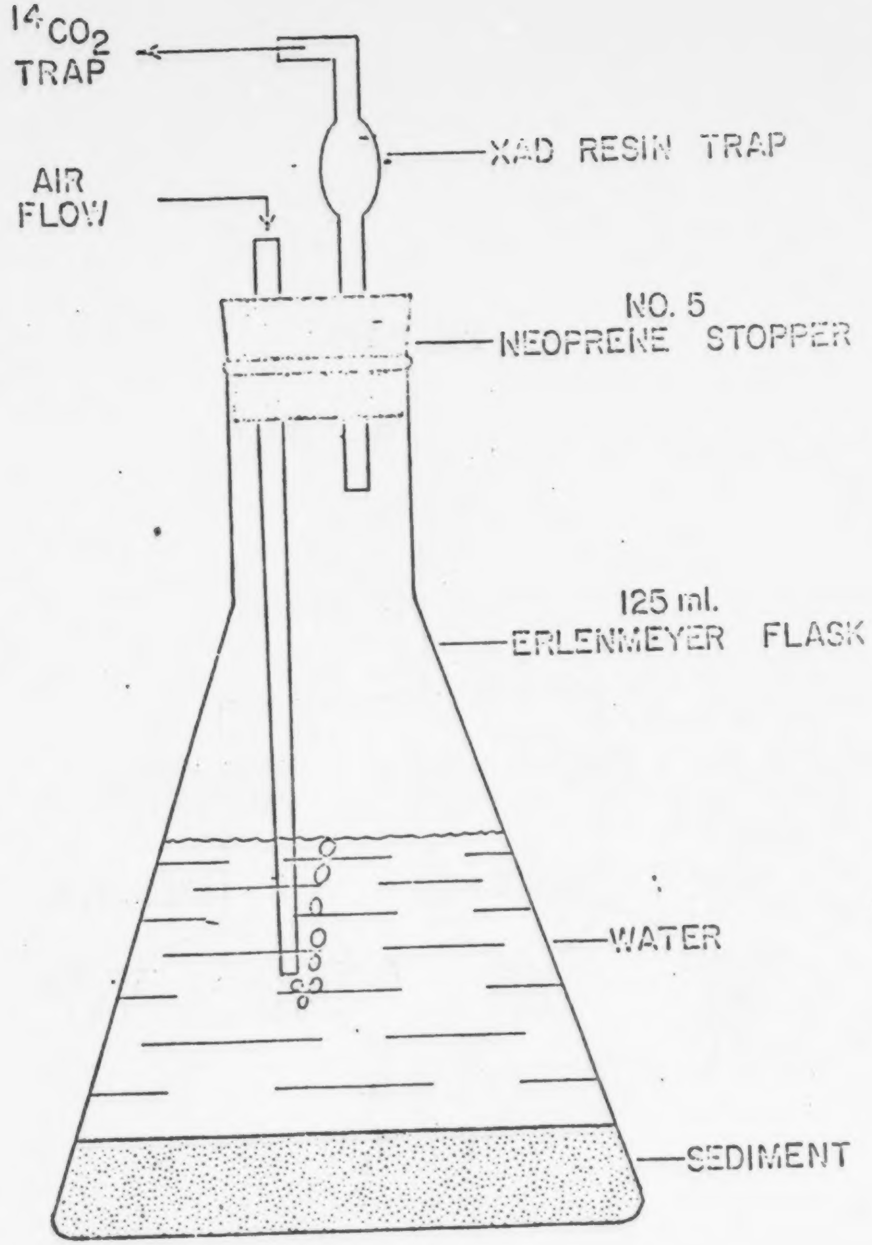
Figure 4. Continuous Flow Microcosm.

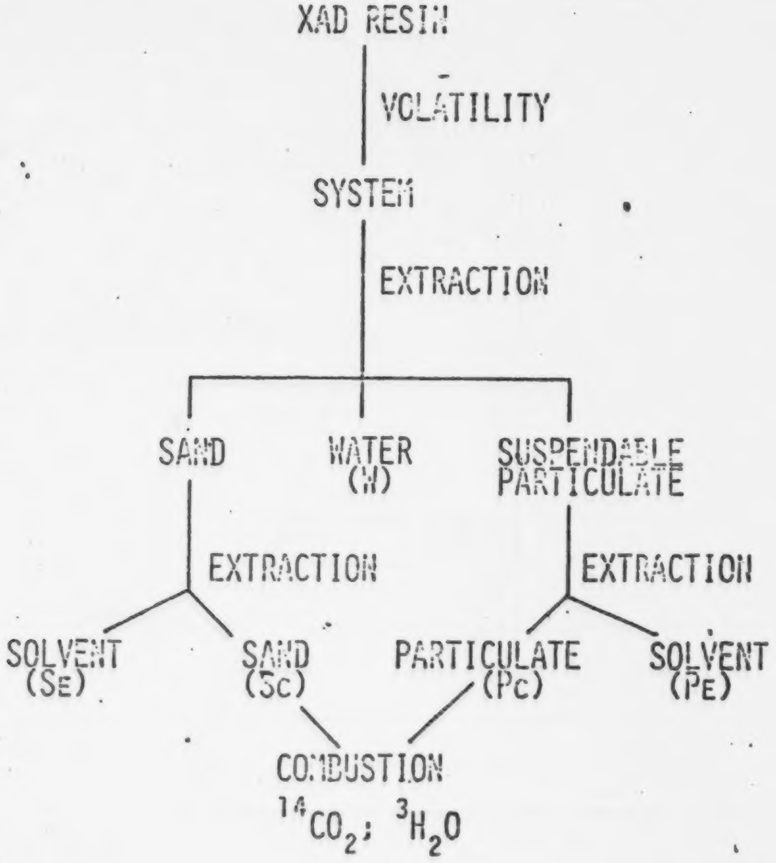
Figure 5. Continuous Flow Systems: Radioactivity Collected in Water Resin Beds.

Figure 6. Continuous Flow Systems: Effect of Flow Rate Change on Radioactivity Export.

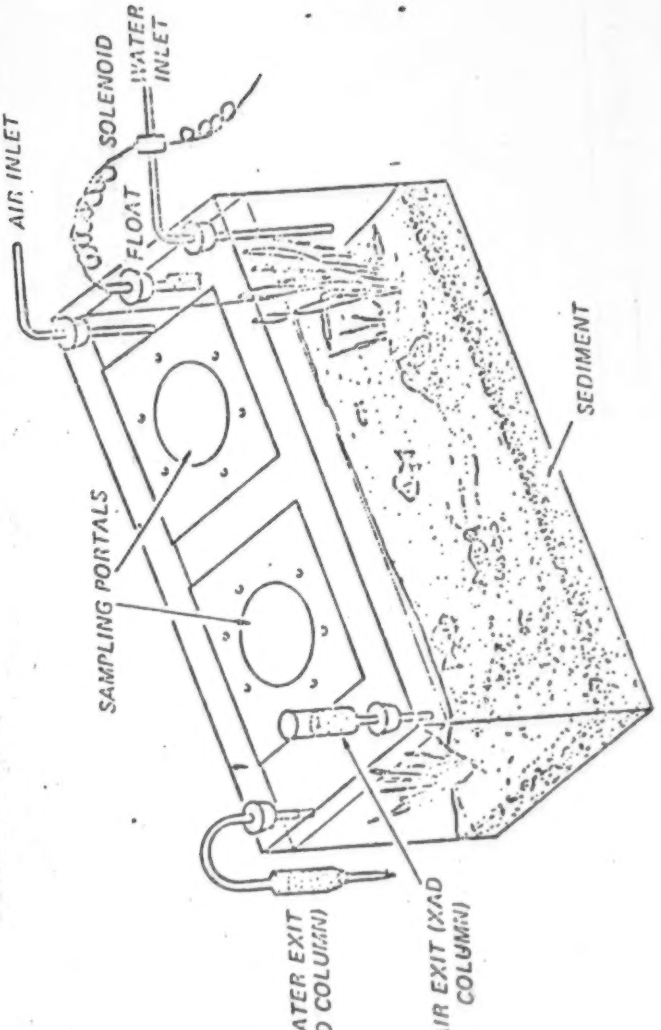

O
Cl
Cl
Cl
Cl
Cl
Cl
Cl
Cl
Cl
Cl

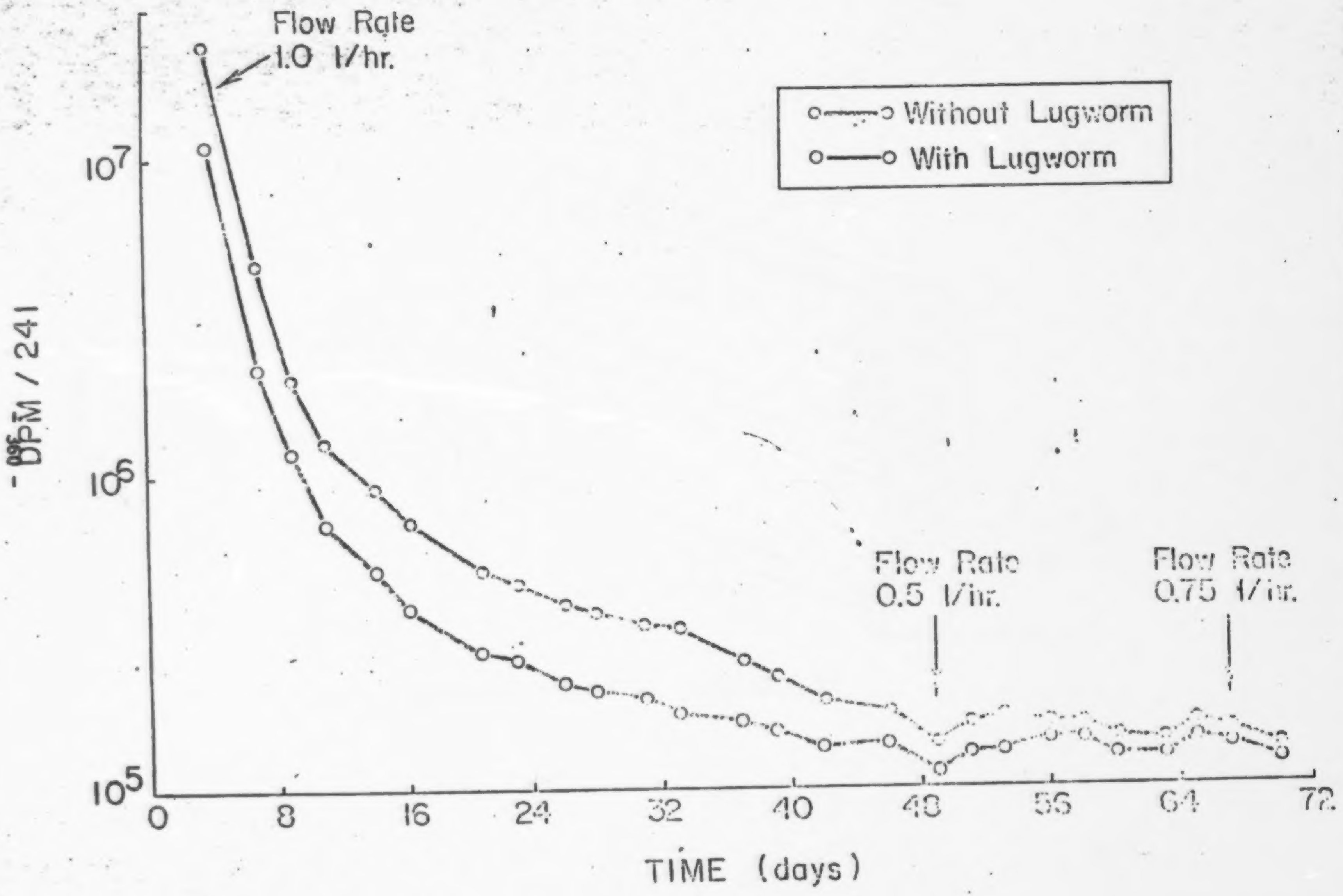
KEPONE

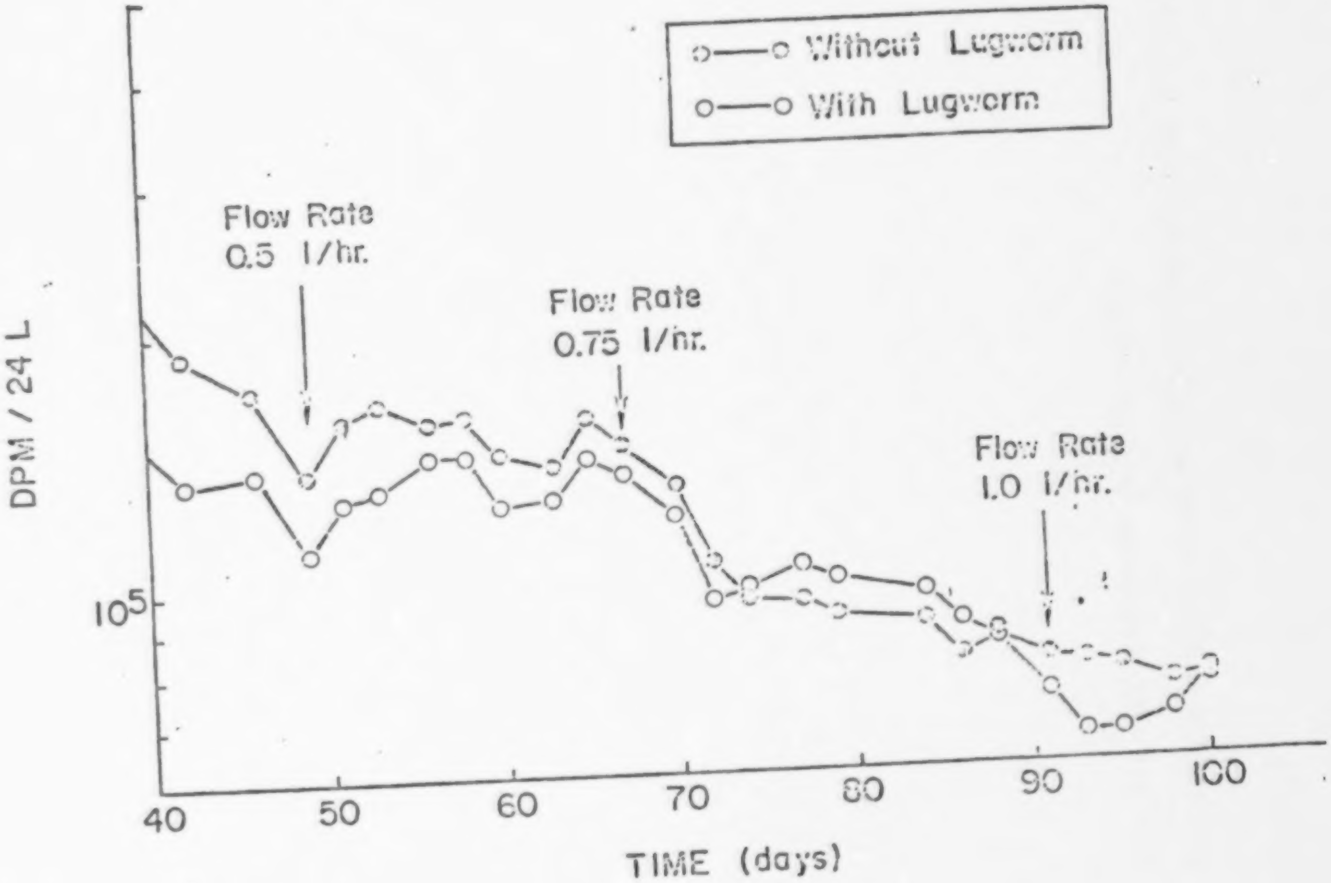

$^{14}CO_2$ TRAP
XAD RESIN TRAP
AIR FLOW
NO. 5 NEOPRENE STOPPER
125 ml. ERLENMEYER FLASK
WATER
SEDIMENT


XAD RESIN
VOLATILITY
SYSTEM
EXTRACTION
SAND
WATER
(W)
SUSPENDABLE
PARTICULATE
EXTRACTION
EXTRACTION
SOLVENT
(SE)
SAND
(SC)
PARTICULATE
(PC)
SOLVENT
(PE)
COMBUSTION
$^{14}CO_2$; $^{3}H_2O$

CONTINUOUS-FLOW MICROCOSM


AIR INLET
FLOAT
SOLENOID
WATER INLET
SAMPLING PORTALS
SEDIMENT
WATER EXIT (XAD COLUMN)
AIR EXIT (XAD COLUMN)


Flow Rate
1.0 l/hr.
Without Lugworm
With Lugworm
Flow Rate
0.5 l/hr.
Flow Rate
0.75 l/hr.
DPM / 241
10^7
10^6
10^5
0
8
16
24
32
40
48
56
64
72
TIME (days)


Without Lugworm
With Lugworm
Flow Rate 0.5 l/hr.
Flow Rate 0.75 l/hr.
Flow Rate 1.0 l/hr.
DPM / 24 L
10^5
40
50
60
70
80
90
100
TIME (days)

ACKNOWLEDGEMENTS

We are indebted to Ronald Dirmeier, Maurice Inkel, Thomas Maziarz, and William Smith for their assistance in this endeavor.

The Role of Sediments in the Storage, Movement and Biological Uptake of Kepone in Estuarine Environments

Annual Report

to:

The Environmental Protection Agency

From:

Robert J. Huggett, Project Manager
The Virginia Institute of Marine Science

For the period
10/20/76 to 10/20/77

Grant Identification Number
R804993010

Preface

Included in this document are three sections which describe the efforts of the Virginia Institute of Marine Science's staff on the Role of Sediments in the Storage, Movement and Biological Uptake of Kepone in Estuarine Environments. The first section is entitled: "Kepone in James River Sediment," by Maynard M. Nichols and Richard C. Trotman. The second, "Kepone Water-Sediment Elutriates," by Robert J. Huggett and the third, "Uptake of Kepone From Suspended Sediments by Oysters, *Rangia* and *Macoma*," is by Dexter S. Haven and Reinaldo Morales-Alamo.

Also attached is a progress report on the EPA funded James River Hydrographical Survey Study which was conducted in the late summer of 1977.

KEPONE IN JAMES RIVER SEDIMENTS

An annual progress report to EPA

by

Maynard M. Nichols and Richard C. Trotman

October 1977

1. Purpose.

This study aims to determine where kepone has accumulated in the bottom sediments; that is, where are the sediment sinks for kepone? A second aim is to trace the routes and rates of transport; that is, what happens to kepone-bound sediment when released from its source? Finally, how long will it take to reduce levels of kepone in the sediment by natural processes?

Results emerging from the study are of use to advise state and federal authorities how to clean-up kepone pollution through natural processes. They provide basic data on sedimentary processes for benthic ecosystem models; they are of use for evaluating the effects of dredging kepone-rich sediments. As a tracer of sediment, kepone provides new information on sediment dispersal and the circulation of fine-grained material in a classic estuary.

2. Highlights of Activities.

Efforts during the period were highlighted by the following:

- Review of James River sediment data to predict fate of kepone for program formulation.

- Presentation of paper on results historical review, First Kepone Seminar, at VIMS, October 1976.
- Preliminary field sampling of surface sediments along length of James in three periods, September, December 1976, and March 1977; 37 to 52 stations sampled during each period; 18 cores obtained.
- Co-ordination conferences with EPA program manager, Dr. Tudor Davies, Gulf Breaze and Virginia State Water Control Board, October through December, 1976.
- Employment of project personnel, Mr. Richard Trotman, completed April 1977; sedimentologic effort in full swing.
- Liason with Battelle Northwest, Dr. Onishi, on field programs and math model formulation.
- Liason with Manhatten College, Dr. D. O'Conner and R. Thomann, concerning formulation of a math model for sediment and kepone transport.
- Development of structure for mathematical model of sediment-kepone transport with Dr. Kuo.
- Formulate plans for suspended sediment-kepone field study, May 1977.
- Follow-up sampling of bottom sediments and selected cores of dredge disposal sites, July 1977. Continued lab analyses of these samples and previous samples.

- Preparation for field study; filters, field equipment, and field labs for processing suspended sediment, June through July 1977.
- Field observations, sampling and measurement of kepone on suspended sediment, currents, and related parameters, August 1977.
- Laboratory analyses of suspended sediment samples, total concentration, organic content, September through October 1977.
- Participation in Second Kepone Seminar and kepone Symposium at the 4th International Conference on Estuaries.
- Follow-up sampling of bed sediments in Hampton Roads and lower Chesapeake Bay in conjunction with closing of area to crabbing; 12 stations occupied.
- Field sampling of bed sediments curtailed in October 1977. Data reduction largely complete.

3. Approach.

Efforts during the period mainly consisted of field sampling, laboratory analyses, and data reduction. First, historical data on kepone and James River sediments were reviewed to identify probable kepone sediment sinks and relative rates of deposition. Sampling stations were sited throughout the estuary in relation to water depth, bathymetry, oyster grounds, deposition patterns, dredge and disposal sites, and in relation to the kepone source.

Field procedures were worked out to sample freshly deposited sediment on the bed as well as in cores at selected sites. Laboratory procedures were set up to process samples for particle size and organic content. The horizontal and vertical distributions of kepone were delineated graphically and evaluated with time over one year in relation to basic information concerning sedimentary processes and transport of fine-grained sediment. An attempt was made to determine from field samples the distribution of kepone in relation to particle size and organic content.

4. Methods and Procedures.

Bed sediments were obtained by a Petersen grab with a 0.05 m^2 bite area or a 7.6 cm (3-inch) diameter corer. The corer was especially constructed for obtaining soft mud with minimal disturbance. Approximately 30 ml of sediment was obtained from the top sediment surface and returned to the laboratory for analyses. Stations were closely positioned by ranging or sextant bearings on buoys and landmarks. Samples were frozen prior to laboratory analyses.

In the laboratory bulk sediment samples were processed for: (1) kepone content, (2) organic matter by loss on ignition, and (3) particle size (percentage sand, silt and clay) by sieving and pipette. Additionally, the sieved fraction, less than 63μ of samples collected in September and December 1976, was analysed for both kepone content and for particle size by a Coulter Counter. Laboratory methods follow conventional procedures described in

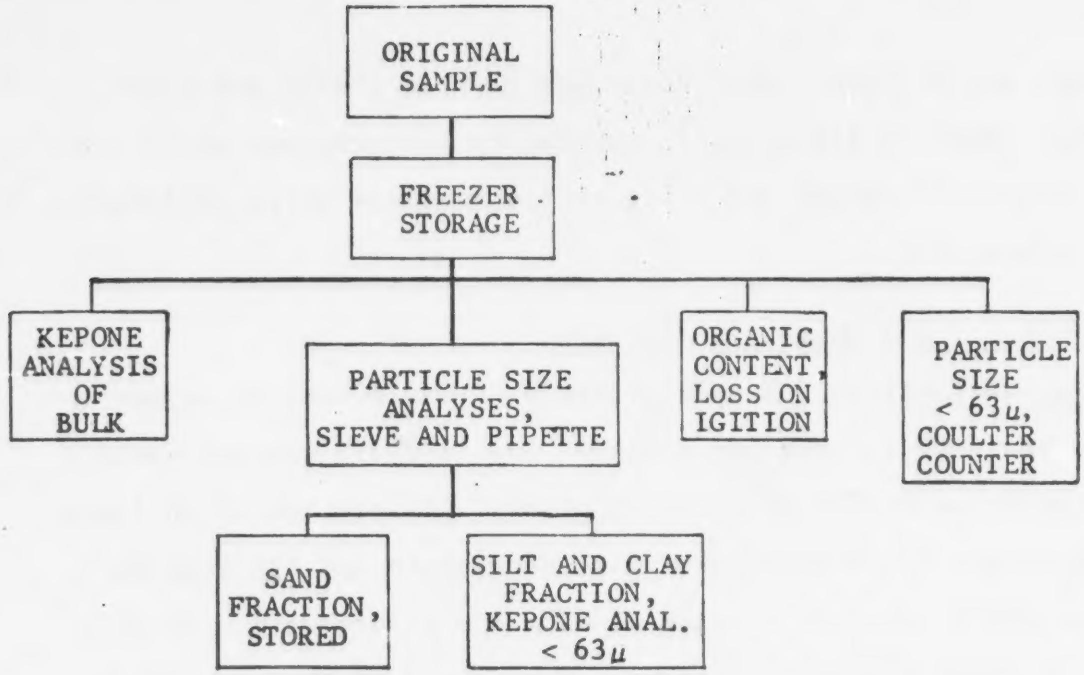

ORIGINAL SAMPLE
FREEZER STORAGE
KEPONE ANALYSIS OF BULK
PARTICLE SIZE ANALYSES, SIEVE AND PIPETTE
ORGANIC CONTENT, LOSS ON IGITION
PARTICLE SIZE < 63μ, COULTER COUNTER
SAND FRACTION, STORED
SILT AND CLAY FRACTION, KEPONE ANAL. < 63μ

Figure 1. Scheme for laboratory processing of bed sediments.

Moncure and Nichols (1968), Standard Methods (1973) and Folk (1961). Details are given in laboratory instructions on file at VIMS sedimentological lab. Figure 1 summarizes steps in laboratory processing.

5. Results and Their Significance.

Spatial Variability. A special study of variations in kepone concentrations in bulk bed sediment over a small spatial range was conducted at two selected stations: (1) station 15 in lower reaches near Wreck Shoal with 3 m water depth and (2) station 40a in middle reaches at buoy 62 with 6 m water depth. At station 15, four samples were taken at random from the top < 2 cm of sediment and of the top < 15 cm of sediment, all from the same grab. Table 1 lists the results. Spatial variations within the 0.05 m^2 area of the grab are relatively small with standard deviations less than ± 7 percent.

Table 1. Variation in kepone concentrations in the top < 2 cm and the top < 15 cm of sediment from a single grab; station 15, June 15, 1977.

Depth Interval	Kepone, ppm	
0-2 cm	0.026	
	0.025	Mean : 0.027
	0.029	Range : 0.025 - 0.029
	0.026	Std. Dev.: ± .002 (± 7%)
0-6 cm	0.012	Mean : 0.013
	0.013	Range : 0.012 - 0.013
	0.013	Std. Dev.: ± .001 (± 8%)

At station 40a one sample was taken of the top < 2 cm of sediment from 10 successive grabs. The grabs were obtained at random while the vessel drifted over distances of 225 m downstream and 135 m upstream from the station. Results of the sampling and analyses (Table 2) indicate a very-wide range of values within a distance less than 230 m. Despite the low bottom relief and small textural differences of the sediment at the site, kepone concentrations ranged as much as 0.41 ppm. When surface samples were taken at random from 12 successive grabs at the same station, number 40a, (Table 2) (an anchor station with an area of about 200 m^2) the kepone concentrations ranged 0.47 ppm with a standard deviation of 44 percent.

Table 2. Spatial variation in kepone concentrations from the top < 2 cm of sediment of successive grabs at station 40a, July 5, 1977 (drift station) and July 20, 1977 (anchor station).

Drift Station		
Downstream 225 m	Upstream 135 m	Anchor Station
0.062	0.021	0.27
0.074	0.025	0.17
0.081	0.029	0.44
0.067	0.023	0.21
0.096	0.017	0.14
0.110	0.013	0.27
0.130	0.027	0.33
0.340	0.033	0.39
0.360	0.029	0.34
0.470	0.023	0.61
		0.61
	Mean : 0.024	0.28
	Range : 0.013 - 0.033	
	Std. Dev.: 0.006 (25%)	
Mean : 0.179		Mean : 0.338
Range : 0.062 - 0.470		Range : 0.14 - 0.61
Std. Dev.: ± 0.151 (± 84%)		Std. Dev.: ± 0.153 (± 44%)

The marked variations are partly due to the sampling process whereby some surface sediment is necessarily washed in the grab or disturbed at depth. However, most local variations are inherent in the bed sediments which are affected by variations in scour and fill, variations in texture and organic matter. Such variations define rather broad limits which may be placed on the kepone distribution as a function of location. They affect "seasonal" distributions inasmuch as the navigational capability of relocating a station is no better than a circle 130 m in diameter.

Distribution of Kepone in Surface Sediments. The sediments from middle reaches are the most contaminated. As shown in Figure 2, average kepone concentrations in bulk bed sediments from the channel (> 4 m depth) are higher between mile 38 and 52 than near the source (mile 63) or farther seaward in the estuary. This is the zone of the turbidity maximum which lies landward of the inner limit of salt intrusion. Suspended sediment concentrations in this zone are higher than elsewhere most of the year.

When longitudinal distributions of kepone are compared for surveys in December 1976, March 1977, and July 1977, there are no significant trends with time. Instead the concentrations are relatively stable within a range of about 0.10 ppm. However, the average levels of concentration from December 1976 through July 1977 in middle reaches (0.15 ppm) are generally

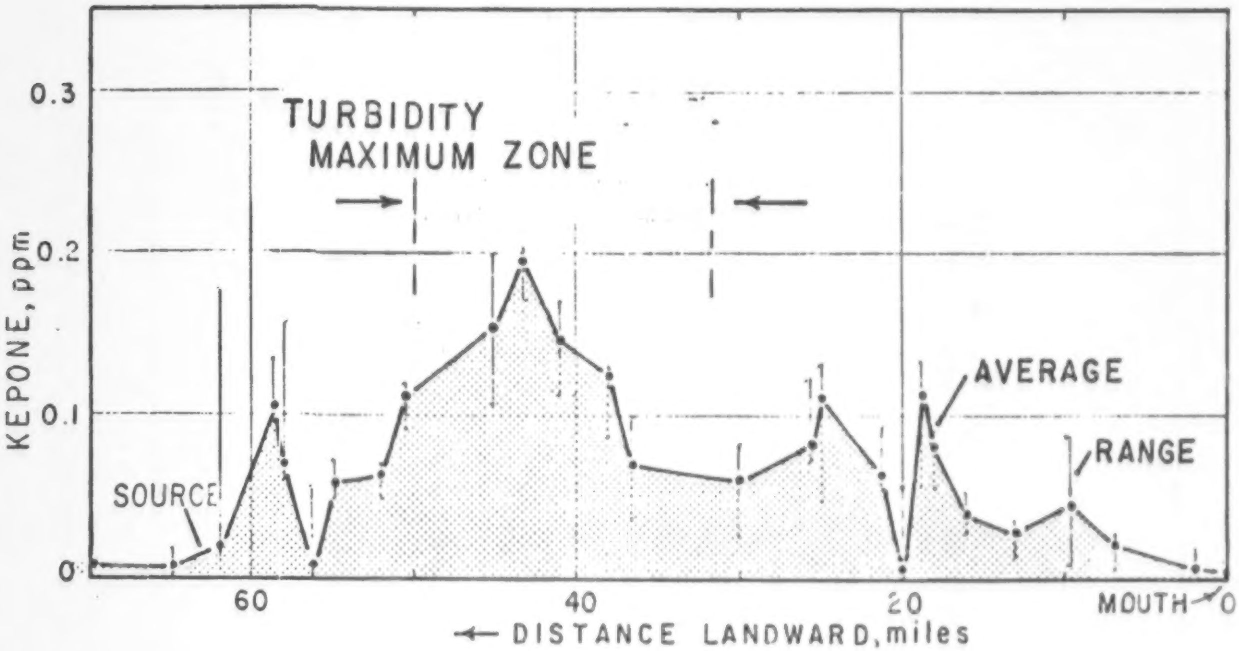


Figure 2. Longitudinal distribution of average kepone concentrations in bed sediments from the channel of the James Estuary; mean of December 1976, March and July 1977 values.

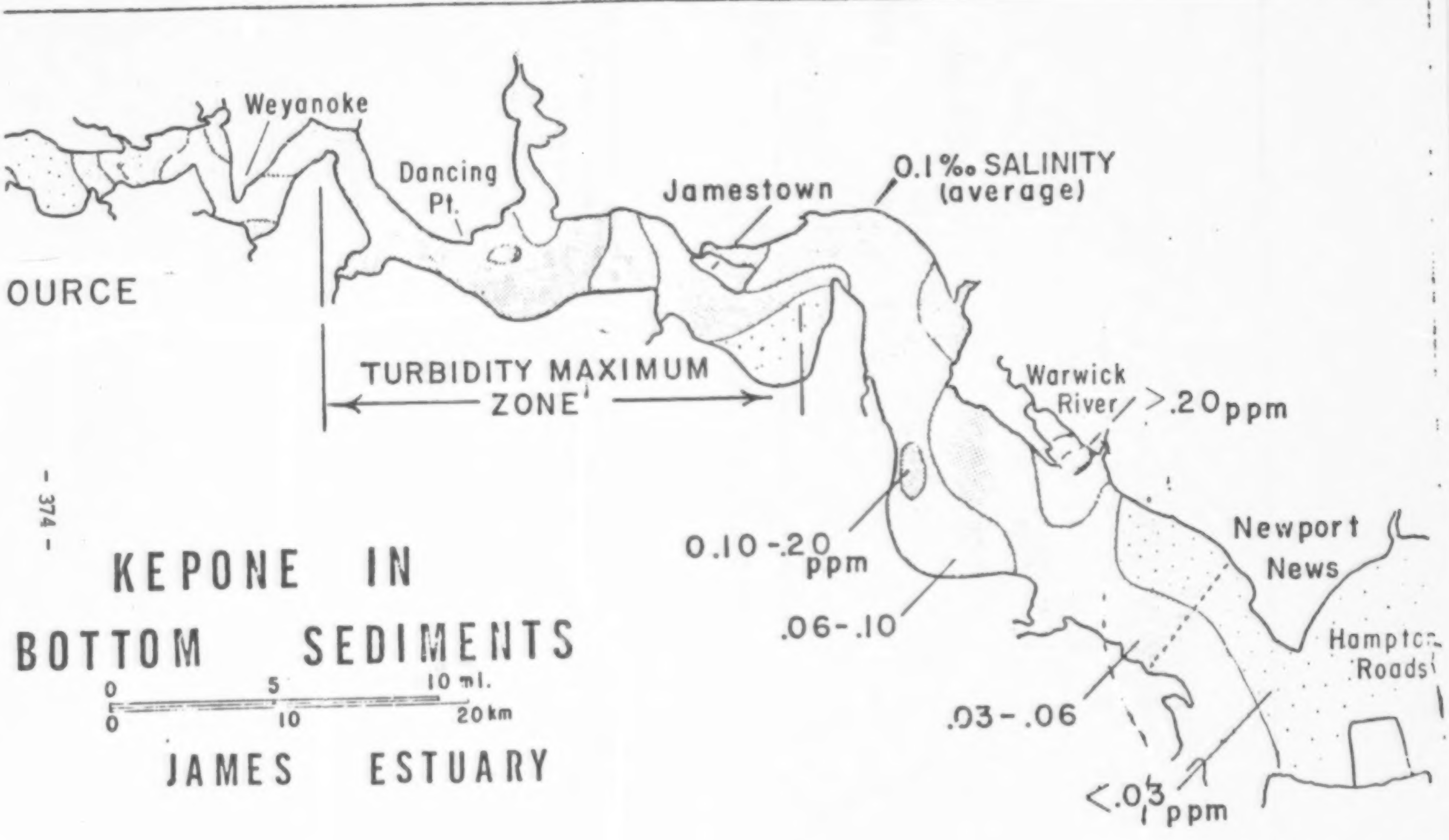

Weyanoke
Dancing Pt.
Jamestown
0.1‰ SALINITY (average)
OURCE
TURBIDITY MAXIMUM ZONE
Warwick River
>.20 ppm
0.10-.20 ppm
.06-.10
Newport News
.03-.06
Hampton Roads
<.03 ppm
KEPONE IN BOTTOM SEDIMENTS
0 5 10 mi.
0 10 20 km
JAMES ESTUARY

Figure 3. Horizontal distribution of average kepone concentrations in bed sediments; mean of December 1976, March and July 1977 values.

lower than those measured earlier by VIMS in September 1976 and by the Corps of Engineers in January 1976 when concentrations were 0.27 to 0.48 ppm.

The zone of high sediment contamination covers both channels and contiguous shoals. As shown in plan view, Figure 3, average concentrations are higher in the reach between Jamestown and Weyanoke than elsewhere. The highest average concentration is in sediment from a shoal off Dancing Point. Elsewhere, concentrations are locally high off mouths of tributary creeks such as Bailey's Creek near the kepone source, Chippokes Creek, The Thorofare, Jamestown and the Warwick River. Substantial concentrations, ranging 0.66 to 1.20 ppm, are found in Burwell Bay. However, concentrations are relatively low in narrowed reaches around Hog Point. Kepone content generally diminishes seaward from Burwell Bay to Hampton Roads where concentrations are less than 0.010 ppm. Twelve sediment samples from lower Chesapeake Bay in September 1977 all had concentrations less than 0.010 ppm.

Distribution of Kepone at Depth in Sediments. Contamination of bed sediments in zones of natural fill (undredged) extends to about 40 cm below the bed surface (Figure 4). Greatest contamination, often exceeding 0.50 ppm, occurs at depths of 10 to 20 cm below the surface. However, in cores from shoals in the shipping channel where sedimentation is locally fast (i.e., 30a), concentrations increase downward to a depth of 60 to 80 cm. This trend reflects the diminished supply of kepone-rich sediment with

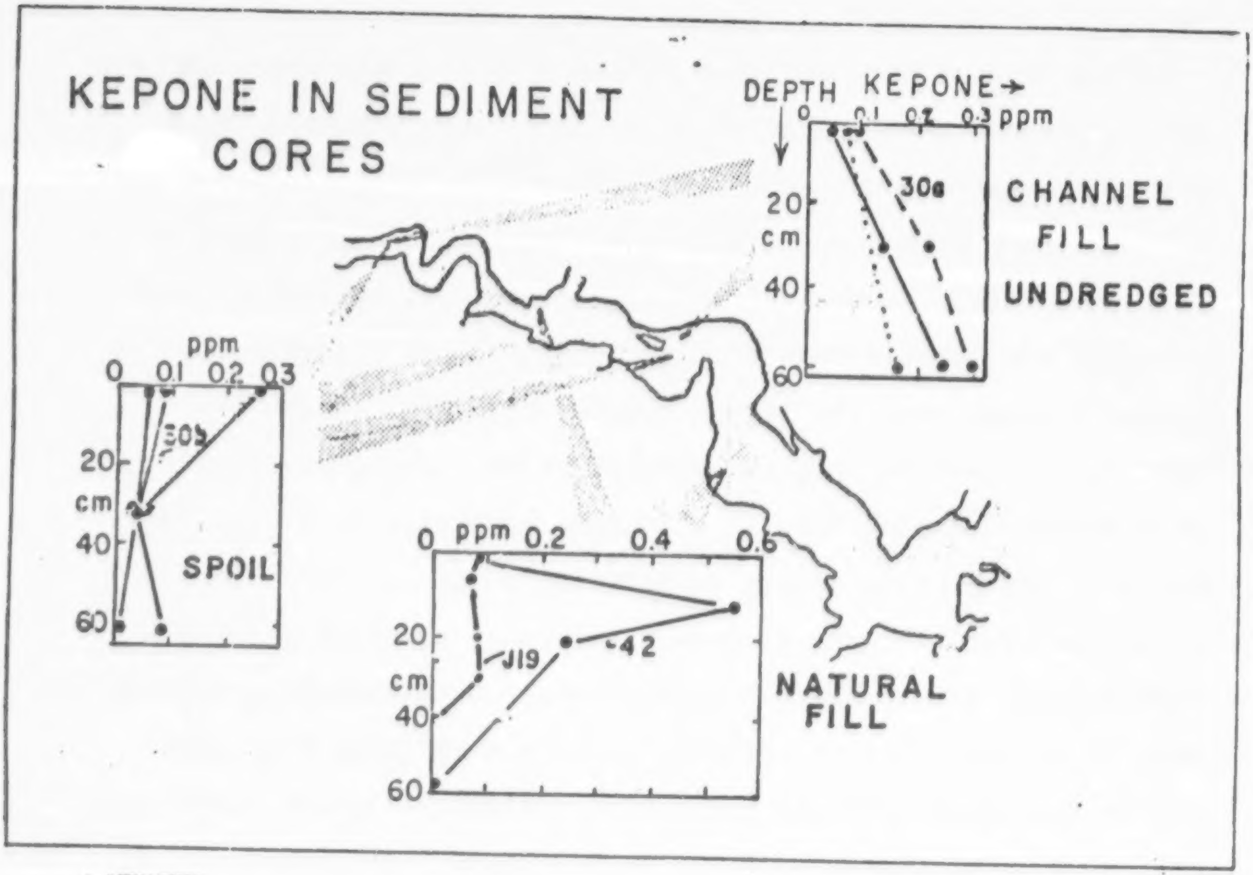


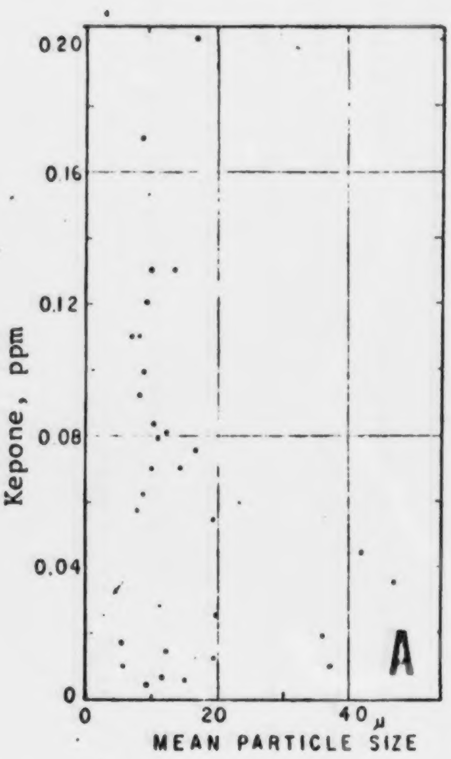
Figure 4. Depth distribution of kepone in cores from selected sites.

time since the Summer of 1975. Kepone content of old dredged material decreases slightly with depth (i.e., cores 41a, 30b, 1.9-7.5). The depth trend results from mixing of sediment during dredging and disposal. The contaminated sediment is most likely mixed and "diluted" by uncontaminated sediment and thus reduces the overall concentration.

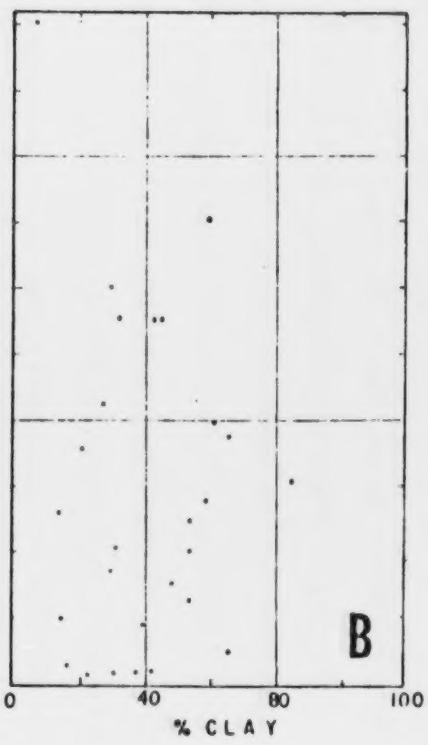
A few samples from the Jamestown-Dancing Point reach collected in May 1967 showed dectable amounts of kepone (.038 and .018 ppm). Although the content is low, the samples suggest that the life span of kepone in the sediments is at least 10 years.

State of Kepone in Sediments. The concentrations of kepone are orders of magnitude greater in the bed sediments than dissolved in estuary water. An indication of the state of kepone storage in the sediments is gained by examining its relation to percent clay content, mean particle size and organic content.

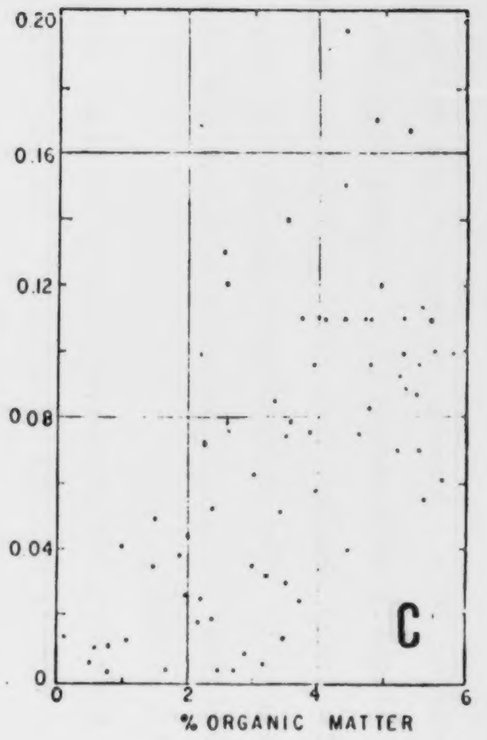
Finer-grained sediments are generally the most contaminated. A plot of mean grain size versus kepone concentrations throughout the estuary (Figure 5a) shows a great deal of scatter. Likewise a plot of percent clay content versus kepone concentrations varies widely (Figure 5b). Part of the scatter results from the great variation in textural types throughout the estuary whereas kepone content partly varies in relation to its source. When kepone content of samples from a single reach of the estuary is considered, however, there is a trend for higher kepone content in the fine-grained sediment with high clay content.



Figures 5a. Kepone content versus mean particle size.



5b. Kepone content versus percent clay content.



5c. Kepone content versus organic matter indicated by loss on ignition.

There is a distinct trend of increasing kepone content with increasing organic content. As shown in Figure 5c, organic-rich sediments have higher kepone content than sediments with low organic content. As expected, samples landward from the kepone source or from zones of scour, display wide scatter. The trend indicates kepone prefers organic matter, either adsorbed on detrital particles or ingested when the organic matter was produced. As organic matter slowly decomposes in the sediment, there is an opportunity for kepone to escape into interstitial or overlying water.

6. Discussion.

Sedimentary Sinks for Kepone. The James Estuary is an environment where much river-borne sediment accumulates. Zones of active deposition may be expected to be areas of relatively high sediment contamination. On the other hand, zones where the bed is scoured into older sediment or zones where river-borne sediments are by-passed, are zones of relatively low contamination. Inasmuch as sedimentary processes are relatively slow, deposition sites are indicators of long-term processes. They are an end product of short-term variations induced by local wave and current transport.

Kepone contamination is generally greatest in sites of active sedimentation: (1) the Jamestown-Dancing Point reach which is also the site of the turbidity maximum, (2) Burwell Bay, and (3) tributary creek mouths. Zones of sedimentation have been

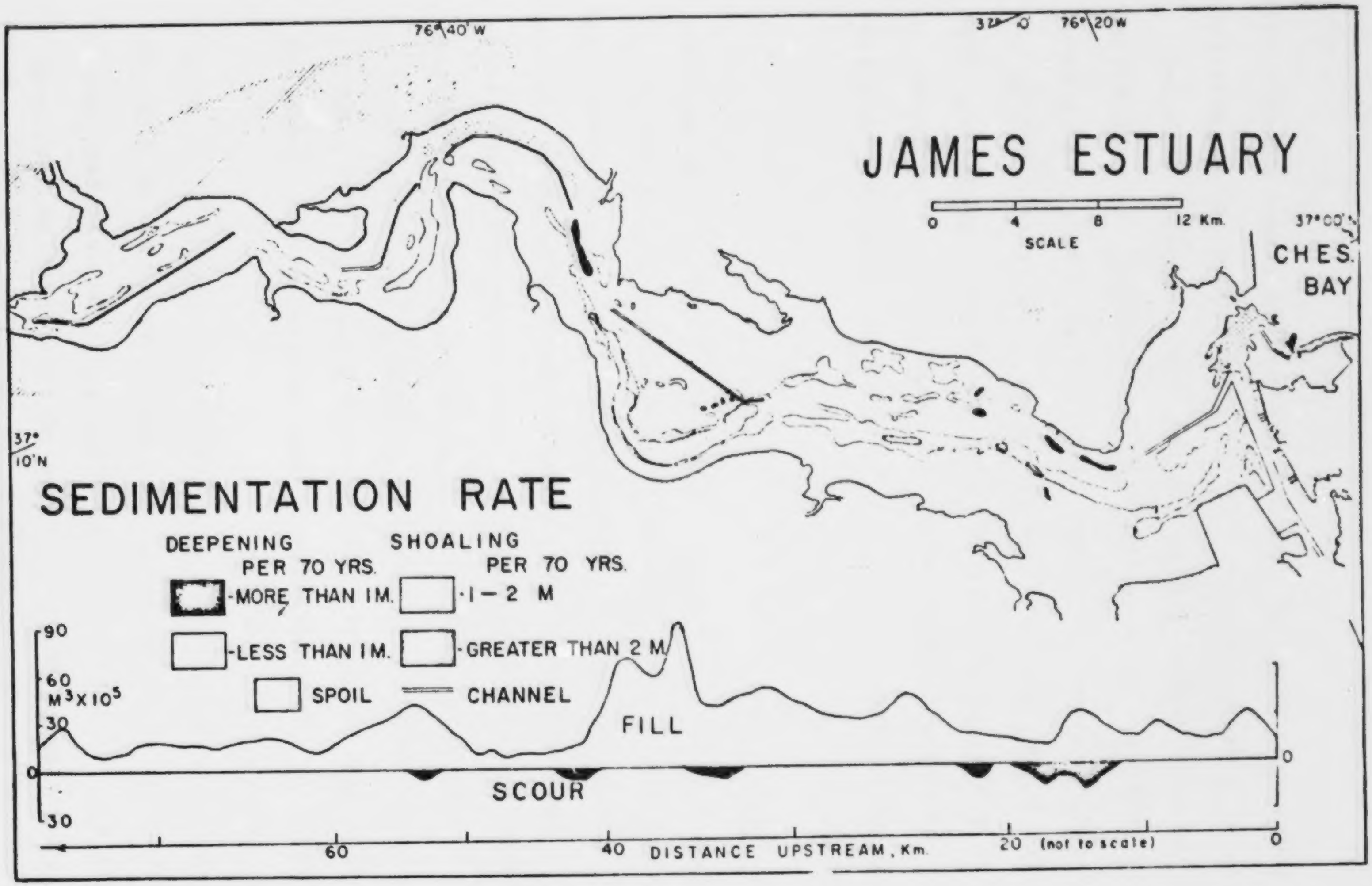

JAMES ESTUARY
76°40' W
37°10'
76°20 W
37°00'
37°
10'N
0
4
8
12 Km.
SCALE
CHES.
BAY
SEDIMENTATION RATE
DEEPENING
PER 70 YRS.
-MORE THAN 1M.
-LESS THAN 1M.
SPOIL
SHOALING
PER 70 YRS.
-1 – 2 M
-GREATER THAN 2 M
CHANNEL
90
60
$M^3 \times 10^5$
30
0
30
FILL
SCOUR
0
60
40
20
0
DISTANCE UPSTREAM, Km
(not to scale)

Figure 6. Sedimentation rates in the James Estuary based on water depth changes over 70 years, from Nichols (1972).

delineated in a former study (Nichols, 1972) (Figure 6) from differences in water depths over 35 and 70 years. The rates of sedimentation within the zones probably change with time but the sites of deposition persist.

Kepone concentrations are locally high off the mouth of Bailey's Creek, the kepone source. However, the main distribution does not display decreasing concentrations with distance away from the source. Instead, the main sink is in the middle estuary, the zone of the turbidity maximum where suspended sediments are trapped and deposited. Sediments in this zone are finer-grained than elsewhere, less than 8μ mean size. Clay content in this zone is also higher than elsewhere in the estuary.

Routes of Transport. From the sedimentation patterns, kepone distributions and existing hydraulic knowledge of the James, it is possible to sketch the probable route of kepone-sediment transport. Both the source of kepone and the major source of suspended sediment come from the same direction, landward or upstream of the estuary. Since the influx of sediment from Bailey's Creek is very small in proportion to the influx of sediment from the main river, it is probable the kepone was mainly introduced in the dissolved form and bound to suspended sediment from the main river. Since the estuary is fresh above Jamestown most of the year, net transport from Hopewell to Jamestown is directed seaward. When suspended sediment reaches the Jamestown area, transport is slowed down because net velocity approaches zero in the null zone at the salt intrusion head. The null zone acts as a dynamic barrier that restricts seaward transport of river-borne suspended sediment carried near the bottom. Only sediment carried near the surface is transported farther seaward through the upper layer. If this sediment settles downward, it is carried back upstream to the null zone by landward density currents through the lower estuarine layer. However, sediment carried over the shoals may escape the estuary through the upper layer especially during floods like Agnes. Nonetheless, the bulk of the sediment load is trapped landward of the null zone. As a tracer of sediment, kepone supports this fact. Most kepone concentrations are located in or above the null zone and they persist with time, both over the short-term, 8 months of sampling, and over the long-term as demonstrated from the distributions at depth in cores. The data indicate that it will take a long time, many years, to reduce levels of kepone in the sediment by natural processes of decay and dispersal. Part of the kepone will be buried by "new" sediment but the most significant reduction will come by "dilution" with uncontaminated sediment introduced during freshets and floods. This trend has already started on the floor of the shipping channel where sedimentation is locally fast.

KEPONE WATER-SEDIMENT ELUTRIATES

Many pollutants have an affinity to sediments which is governed by the surface charges on particles. This is particularly true for some of the trace metals - such as zinc - with the clay mineral portion of the sediments. The magnitudes of the surface charges are affected by pH and salinity (Parks, 1967). Therefore, it was necessary to determine if Kepone behaved in a similar manner because, in the James River, both the estuarine and the tidal fresh water portions with their wide ranges of pH and salinity were contaminated by the pesticide. As well the distribution of Kepone in the bottom sediments of the James show a marked increase in that portion usually in the vicinity of the freshwater - saltwater interface. At this boundary the waters change from fresh, (salinity <0.5‰) to saline, (salinities 0.5‰ to 20 - 25‰). Also in this region the pH of the water increases from near 7 to 8 due to the buffering capacity of seawater. With these abrupt changes in pH and salinity coinciding with the change in Kepone concentration, it appeared possible that fresh water sediments, highly contaminated with the pesticide, were being "extracted" by estuarine waters as they traversed this boundary progressing seaward or that Kepone in solution was not adsorbed by sediments in saline waters. Therefore, experiments were conducted in the laboratory to determine the extractibility of sediment-Kepone by waters with varying ranges of salinity and pH.

The experimental design included two phases. The first phase was to determine the accuracy and precision of the analysis of water for dissolved Kepone and the second phase was to determine the amount of Kepone removed from contaminated freshwater sediments by waters with pH's ranging from 6 to 9 and salinities of <0.5‰ and 20‰.

These ranges of pH's and salinities bracket those found in the James River.

Phase I, Water-Kepone Analysis

The method utilized for the Kepone-water extraction was one developed by The Environmental Protection Agency, Research Triangle Park (1975). It involves liquid extraction using benzene as the organic solvent. The extractions are carried out in seperatory funnels with 3 successive treatments of the same water with benzene at a ratio of 1:10 benzene to water. The extracts are combined and then dried by passing them through anhydrous sodium sulfate. The combined extracts are then analyzed by electron capture gas chromatography.

To check the efficiency and accuracy of the procedure, Kepone free water, (obtained either from Kepone noncontaminated estuaries such as the York or from laboratory deionized-double distilled stocks), was spiked with known amounts of Kepone, extracted and analyzed (Table I).

Phase II, Water Extraction of Kepone From Sediments.

The experimental design for this phase involved subjecting Kepone contaminated sediments from the James River, obtained from the fresh water portion, near Hopewell, to waters with varying pH's and salinities. The salinities were either fresh, (0.06‰), obtained from the James River or saline, (19.5‰), gotten from the mouth of the York River at the Virginia Institute of Marine Science's facility. The pH's of these waters were adjusted to the desired levels by addition of either reagent grades of hydrochloric acid or sodium hydroxide.

After the desired pH and salinity were achieved, a portion of wet sediment (100 g   ) was placed in a flask and the water (250 ml) was added and the mixture was agitated with a Wrist-Action Shaker for 1 hr. Following this the sediments were separated by centrifugation and the supernatant water was extracted for dissolved Kepone by the method previously described in the Phase I section of this report.

In all, 36 separate extraction were analyzed and the resulting water Kepone concentrations were compared to that in the exposed sediments. The comparisons are reported as the percent removed by a water of a given pH and salinity in Table II.

Discussion:

The data from Phase I clearly show that the Benzene method of extracting Kepone from water yields approximately 85% or better of the amount of the pesticide from solutions spiked at 1 ppb to 10 ppb. However, at concentrations below 1 ppb the efficiency drops greatly - for instance, 64% yield at 0.5 ppb. These yields can be used to judge the accuracy obtained for Kepone analyses of water by this method. The precision estimates can be seen from the standard deviations which show ± 14% or better for spiked solutions of 1 to 10 ppb. The precision of the method for concentrations of 0.5 ppb are in the same range which suggests that a portion of the "spike" may be sorbed to the walls of the glassware or lost by some other means.

Attempts were made to try solvents other than benzene, for extraction, (ethyl acetate - toluene, methylene chloride) but with the similar results - dissolved Kepone at concentrations less than 1 ppb may be 100% in error.

Since only at the 10 ppb Kepone concentration were the effect varying salinities on the analysis compared, it is risky to judge salinity effects on the method. Evenso, there is no obvious effect using natural waters of 0.06 and 19.5‰.

The extraction experiments, the results of which are given in Table II and Figure 1, show that there is no apparent affect of either salinity or pH, within the ranges used which approximate those found in the James River, on the extractibility of Kepone from sediments by water. It must be kept in mind, however, that the amounts of Kepone extracted were in the tenths of ppb range. Since the analytical methodology is less than ideal at these concentrations some differences could go undetected. Figure I shows that all results are within 2 standard errors of each other which implies no difference at the 95% confidence interval.

The data indicate that, if the analyses are correct, the partitioning coefficient of Kepone from sediment to water is approximately 6×10^{-4}, irrespective of natural ranges of pH and salinity. It follows then, that the relatively high concentrations of Kepone at the fresh water-salt water interface and upstream are likely due to the turbidity maximum (mentioned in the sediment section) rather than chemical factors such as partitioning.

References

Environmental Protection Agency, 1975, Preliminary Report on Kepone levels from Hopewell, Va area. Briefing at Research Triangle Park, North Carolina

Parks, G. A., 1967. Aqueous Surface Chemistry of Oxides and Complex Oxide Minerals: Equilibrium Concepts in Natural Water Systems, p. 121-160. In Gould, F. (Ed), Advances in Chemistry, Series 67. American Chemical Society Publications.

TABLE I

Extraction Efficiencies of Kepone from Water by the Benzene Method

Salinity	Adjusted pH	Kepone Spiked Concentration	% Recovery
0%, Deionized H_2O	7.0	10ppb	96%
"	"	"	99%
"	"	5ppb	87%
"	"	"	90%
"	"	"	78%
"	"	"	94%
"	"	"	95%
"	"	1ppb	97%
"	"	"	72%
"	"	"	93%
"	"	"	69%
"	"	"	93%
"	"	"	56%
"	"	"	102%
"	"	"	85%
"	"	"	86%
"	"	"	96%
"	"	"	83%
"	"	0.5ppm	72%
"	"	"	51%
"	"	"	67%
"	"	"	71%
"	"	"	67%
"	"	"	55%
"	"	"	80%
"	"	"	48%
"	"	"	69%
0.06% James R. H_2O	7.0	10ppb	86%
"	"	"	99%
"	"	"	92%
"	"	"	85%
"	"	"	83%
"	"	"	77%
"	"	"	76%

TABLE I (continued)

Salinity	Adjusted pH	Kepone Spiked Concentration	% Recovery
19.5% York R. H_2O	8.0	10ppb	74%
"	"	"	85%
"	"	"	73%
"	"	"	99%
"	"	"	74%
"	"	"	103%
"	"	"	99%

TABLE I

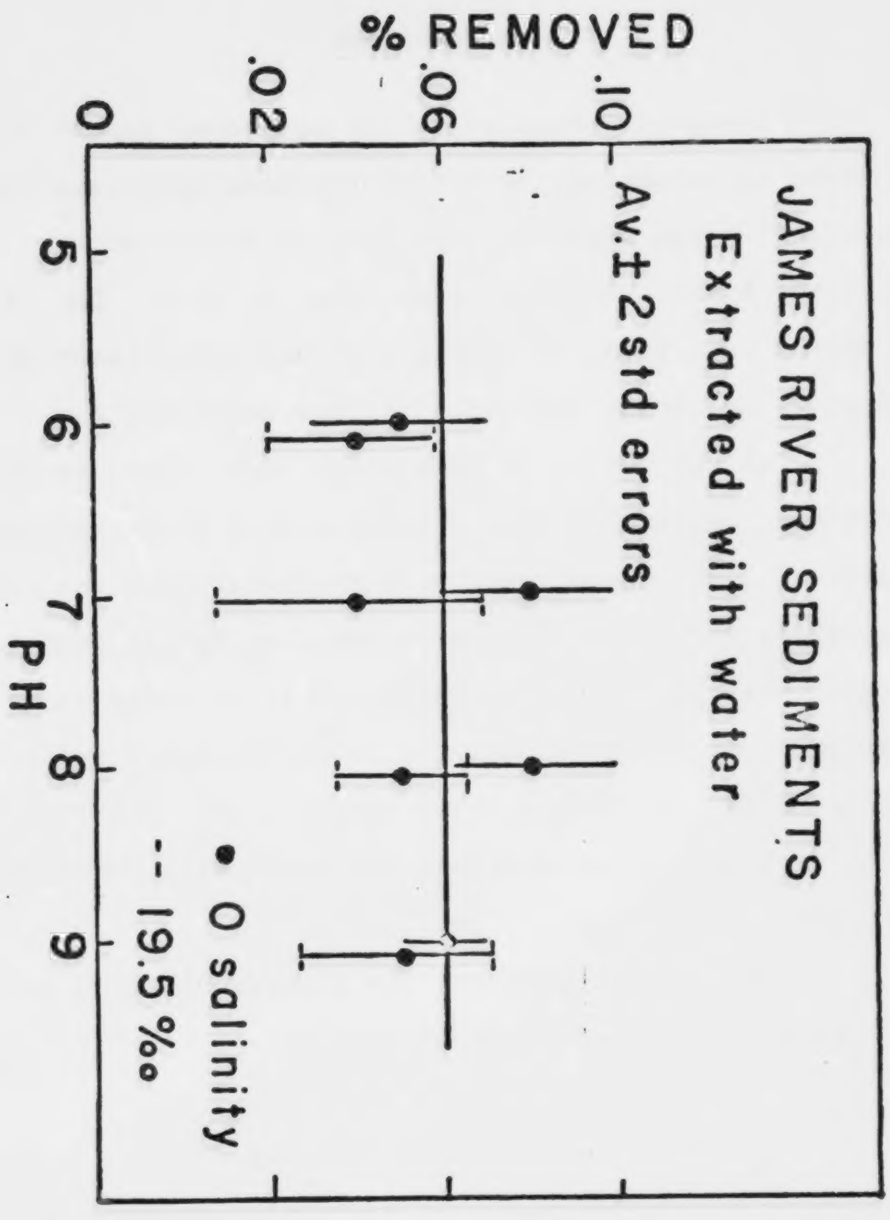
Summary

Salinity	Adjusted pH	Kepone Spiked Concentration	Average yield And Standard dev.
Deionized + Distilled	7.0	10ppb	98 ± 2%
"	"	5ppb	89 ± 7%
"	"	1ppb	85 ± 14%
"	"	0.5ppb	64 ± 11%
0.06% James River H_2O	7.0	10ppb	85 ± 8%
19.5% York River H 0	8.0	10ppb	87 ± 13%

Elutriate Results

Salinity	(Sediment ± ppm Kepone) pH	% Removed	± Sd
0.06‰	6.0	0.04%	STD. ERROR - 0.01
"	"	0.06%	0.05 ± 0.01% of total Kepone in sediment recovered at a pH 6.0 + 0.06‰
"	7.0	0.11	
"	"	0.11	
"	"	0.09	
"	"	0.12	0.08 ± 0.04% of total Kepone in sediment recovered at a pH 7.0 + 0.06
"	"	<0.01	
"	"	0.07	
"	"	0.06	
"	"	0.06	STANDARD ERROR 0.01
"	"	0.11	
"	8.0	0.06	
"	"	0.09	0.08 ± .02% of total Kepone in sediment recovered at pH 8.0 + 0.06‰
"	"	0.09	
			STANDARD ERROR 0.01
"	9.0	0.05	0.06 ± 0.01% of total Kepone in sediment recovered at pH 9.0 + 0.06‰
"	"	0.06	
			STANDARD ERROR 0.005
19.5‰	5.0	0.03	0.03 ± ? %
"	6.0	0.04	0.04 ± 0.02% of total Kepone in sediment recovered at pH 6 + 19.5‰
"	"	0.06	
"	"	0.03	
			STANDARD ERROR 0.009
"	7.0	0.02	STANDARD ERROR 0.015
"	"	0.07	0.04 ± 0.03% of total Kepone in sediment recovered at pH 7 & 19.5‰
"	"	0.04	

"	8.0	0.09	
"	"	0.06	
"	"	0.05	
"	"	0.06	0.05 ± 0.02% of total Kepone in sediment recovered at pH 8.0 + 19.5%
"	"	<0.01	
"	"	0.05	
"	"	0.04	
"	"	0.06	STANDARD ERROR 0.007
"	"	0.02	
"	"	0.05	
"	9.0	0.07	
"	"	0.05	0.05 ± 0.02% of total Kepone in sediment recovered at pH 9 + 19.5%
"	"	0.03	
			STANDARD ERROR 0.012


JAMES RIVER SEDIMENTS
Extracted with water
Av. ± 2 std errors
● 0 salinity
-- 19.5 ‰
% REMOVED
0
.02
.06
.10
5
6
7
8
9
PH

UPTAKE OF KEPONE FROM SUSPENDED SEDIMENTS BY OYSTERS, RANGIA AND MACOMA

Introduction

Laboratory studies on the uptake of Kepone from sediments in suspension by bottom-dwelling organisms were undertaken by the Virginia Institute of Marine Science at Gloucester Point, Virginia on December 1, 1976. The first two months were spent in acquisition and preparation of laboratory equipment and space for the experiments.

In the period of time since then, three series of laboratory experiments were conducted with three species of bivalves. Eight experiments were completed with the oyster *Crassostrea virginica*, five with the clam *Rangia cuneata* and one with the clam *Macoma balthica*. Most of these experiments involved exposure of the animals to contaminated sediments in suspension. In two of them, however, the animals were placed in a bed of contaminated sediments with uncontaminated river water flowing over them.

This report presents the results of three series of experiments followed by a discussion.

Materials and Methods

Apparatus

A diagram of the basic arrangement of the apparatus used to conduct these experiments is shown on Figure 1. The units labelled A through D were used only during the first series of experiments when ambient river water temperature was below 10 C most of the time. York River water was piped into a constantly-overflowing box (A) from which it was pumped through heat exchangers (C) into a rectangular cascading trough (D). The latter served to allow bubbles created by the escape of dissolved gases to dissipate before reaching the animal trays. This section of the system was not used in the last two series of experiments when river water temperatures were above 10 C. Then, York River water was piped directly into a rectangular trough (E) which was suspended from the ceiling directly above the wet table that held the experimental trays. Water depth in the trough was maintained at 20 cm by a drain standpipe of that height.

Water to supply the experimental trays was siphoned out of trough E with plastic tubing. In the first series of experiments water flow rates were controlled by inserting glass flowmeters (F) in the tubing siphons ahead of the mixing chambers (I). In the last two series of experiments the flowmeters were omitted. Instead, flows were regulated by the bore size of the plastic tubing used for siphons. This eliminated constrictions in the tubing caused by adjustable clamps which enhanced flow interruptions due to clogging. Siphons were cleaned daily and flow measurements made before and after the siphons were cleaned.

Water from the siphons entered a rectangular mixing chamber made of acrylic plastic (I), 25 cm in length, 16 cm in width and 14 cm in height, through a smaller chamber (2 cm long, 3.5 cm wide and 14 cm high). The smaller chamber was connected to the larger one by a circular opening with a 2 cm diameter. Contaminated sediment suspensions also entered the mixing chamber through the same small chamber. Stock suspensions were kept well mixed in flasks (H) by magnetic stirrers (J). They were metered into the mixing chamber at a constant rate by peristaltic pumps (G).

River water and sediment suspensions were mixed in the mixing chamber by magnetic stirrers. Observation showed that the mixing was complete before the mixture flowed out of the mixing chamber. Sedimentation in the chamber was negligible. The diluted sediment suspensions flowed into the experimental trays (K) through a standpipe located at the end opposite to the one through which water and sediments entered the chamber. The system set up was the same for trays holding control animals except for elimination of components G and H.

In experiments with the clam Rangia cuneata, York River water salinity was reduced to between 5 and 6°/oo by addition of fresh ground water pumped from a shallow well. A second rectangular trough (P) was suspended below the one receiving York River water (E). York River water was siphoned (Q) from trough E into trough P. Fresh water was also piped into a cascading trough similar to D to eliminate gas bubbles generated by the change in pressure the ground water was subjected to before it flowed into trough P. Water of the resulting lower salinity was then siphoned into the trays holding Rangia clams following the same system setup labelled F through K in Figure 1.

Figure 2 shows a partial view of the apparatus used in the series of experiments.

A system of sediment traps was used to insure that no contaminated sediments from our experiments escaped into the floor drain which emptied into the York River. The first component was the wet table on which the experimental trays were set (L in Figure 1). A standpipe about 2.5 cm high inserted in the drain hole of the wet table converted the table into a sediment trap. A plastic circular tank (50 cm high and 30 cm in diameter) received water from the wet table through a pipe reaching close to the bottom. The tank overflowed near its top into a series of three rectangular boxes (114 cm long and 25 cm wide), each with a 15 cm high standpipe overflow. The third box overflowed into the floor drain. The sediments and other excess solids obtained in the experiments were collected in carboys for disposal.

Experimental Trays

Two types of trays were used to hold experimental animals. In most experiments, a tray made of acrylic plastic 49 cm long, 26 cm wide, and 8 cm high, were used. The overflow end was 6 cm high and that also was the depth of the water in the tray. This tray was not compartmentalized and the animals laid directly on the bottom (Figure 3).

A larger acrylic plastic tray, 81 cm long, 54 cm wide and 8 cm deep was used in the third series of experiments to hold oysters whose biodeposits were collected. A baffle at the overflow end of the tray maintained water level at a depth of 6.5 cm. These trays were divided into 25 compartments by plastic strips 2.5 cm high. Each compartment held one oyster. The compartments facilitated separation and collection of biodeposits.

Biodeposits

Biodeposits produced by oysters receiving contaminated sediments in suspension in the large trays were collected every day with a bulb pipette. The aggregates collected at the end of each weekly period were then analyzed for Kepone. Every time biodeposits were collected, sediments settling out by gravity in the same tray were also collected and the weekly accumulation also analyzed for Kepone contents. Each day, after biodeposits and sediments had been collected, every compartment was cleaned of any remaining sediments.

Animals Buried In Mud

A modification to the manner usually used to expose animals to contaminated sediments, i.e., by flowing sediment suspensions over them, was introduced in the third series of experiments. Oysters and *Rangia* were buried partially and fully, respectively, in beds of contaminated sediments held in the smaller of the trays described above (Figure 4). The sediment bed was 4 to 5 cm deep. It was made up of unsieved sediments from the same batch used in simultaneous experiments with flowing suspended sediments.

Oysters were pressed into the sediments at about a 30° angle. Up to one-third of their height was below the sediment surface level. The valve area over the gills protruded above the sediment surface. Rangia were pressed into the mud so that almost the whole animal was below the sediment surface level. Within several hours they had buried themselves fully into the sediment so that only their siphons showed. Water flowing over the animals and the sediment bed had no sediments added to it and was approximately two to three cm deep.

Source of Experimental Animals

The animals used were obtained from areas to be free of Kepone^{R}. Rangia and Macoma were collected from the Rappahannock River and oysters came from the Piankatank River. All three species were acclimated to the experimental temperatures and salinities under flowing-water conditions at least one week prior to use. Analysis before start of each experiment showed them to be free of contamination with Kepone^{R}.

Preparation of Sediment Suspension

Figure 5 presents a flow chart outline of the steps taken in preparation of Kepone^{R} contaminated sediment suspensions. All contaminated sediments were collected with a sediment grab sampler at Jordan Point, in the James River at Hopewell and represented the top 6 cm of the bottom. They were transported to the laboratory in 2 or 3 large plastic bags each containing about 20 kg of material. The contents of each bag was mixed and transferred to smaller bags in fractions of approximately 500 ml in volume. The smaller bags were stored in a freezer until needed. Only sediments collected on the same date were used in any one series of experiments.

When needed, a bag of sediments was thawed, mixed with well water and shaken mechanically in flasks for 12 hours or more. The sediments were then wet-sieved through a 63 u and the resulting suspension diluted up to 7000 ml with well water. This volume was labelled as stock suspension and given an identification number. It was maintained in suspension by continuous agitation with a magnetic stirrer and bar. Subsequently, to insure homogeneity in dosage, it was divided into measured portions by alternately siphoning a small volume into each of six containers and repeating the cycle until each container had been filled to the desired volume.

The samples in two of the containers, with volumes of approximately 400 and 200 ml, were used to determine the concentration of Kepone in the suspension and the dry weight per unit volume of the sediments in the suspension, respectively. The suspension in the other four containers, usually with volumes of 1200 and 1600 ml, was the material to be introduced into the trays holding experimental animals. The suspensions in the four containers were diluted in a ratio of 1:4 and pumped into the mixing chambers.

Sampling of Animals in Trays

Samples of the animals were analyzed for Kepone at the start of each experiment and at approximately weekly intervals thereafter for the four-weeks duration of the experiment. Each sample consisted usually of three or four animals and at times of up to eight individuals in the case of oysters and *Rangia*. In the case of *Macoma* the number ranged between seven and fifteen. The shell of each animal was carefully scrubbed after removal from the tray.

Kepone Analysis

Analysis of all samples from concentration of Kepone were done by personnel of the Department of Ecology and Pollution in their laboratories. The method used was soxhlet extraction, fluorosil cleanup and electron-capture gas cromatography.

Determination of Kepone Concentration in Sediments

The concentration of Kepone in the diluted sediment suspension flowing over the experimental animals was determined by computation of the product of four factors:

$$K_c = (s_c)\ (k_c)\ (d_1)\ (d_2)$$

where

K_c = computed Kepone concentration in diluted suspension, in ppb

s_c = sediment dry weight per unit volume in stock suspension, in Kg/l

k_c = Kepone concentration determined analytically

d_1 = factor by which stock suspension was diluted prior to being pumped into mixing chambers.

d_2 = factor by which the suspension being pumped into mixing chambers was diluted; determined by the flow rate at which it was being pumped and the flow rate of York River water flowing simultaneously into the mixing chamber.

The factor d_2 was controlled in each experiment by selection of peristaltic pump settings that would deliver a desired flow rate of the sediment suspension into the mixing chamber. The flow of river water into the mixing chamber was also adjusted to the desired rate. Flow of river water was maintained relatively constant while the flow rate of contaminated sediments was adjusted so that trays would receive sediment suspensions at different rates.

Some trays received what was labelled as low concentrations of sediment (and, therefore, also of Kepone) while others received medium and high concentrations. Throughout an experiment the ratio between low, medium and high concentrations remained fairly constant even though Kepone concentrations in stock suspensions were variable. As a result, the concentrations labelled as low were always significantly lower than those labelled medium or high. The separation of low concentrations from medium and high ones is the main distinction made between concentrations in this report.

Preparation of Data for Analysis

In the course of one series of experiments between 30 and 40 different stock suspensions (500 ml bags) were used.

Sediment concentration and Kepone concentration varied from one stock suspension to another. Consequently, the experimental animals in any one tray were not being exposed to a constant concentration of Kepone during the time they were held in the trays. However, throughout the duration of an experiment, the ratio between low, medium and high concentrations remained fairly constant. As an aid in interpretation of results, a weighted mean hourly concentration was computed for each of the weekly periods as the sum of the products of the concentration in each stock suspension and the length of time (in hours) that particular suspension was used, divided by the total number of hours in the weekly period. Included in these computations, were short intervals during which, for a variety of reasons, no sediments were being added to the water flowing over the animals. These intervals were usually few and anywhere from 15 min to 2 hour in duration. Also involved was a final interval of eight to nine hours at the end of a weekly period when the animals only received river water to allow them to eliminate material held in their digestive tract.

Despite the mixing done before the sediment sample was divided into 500 ml fractions, differences in sediment and Kepone concentrations from one stock to another were sometimes large. Thus, differences of significant magnitude were encountered sometimes between the mean hourly concentrations for the different weekly periods in one experiment. Since there was a high correlation between the concentration of

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Kepone in oyster meats and its concentration in the sediments, and to eliminate the effect of the variations between stock suspensions, the values for oyster meats were normalized by re-computation based on the mean hourly concentration of Kepone in the sediments over the approximately four-weeks duration of experiment. The new values represent the concentration of Kepone expected in oyster meats if the concentration in sediments was constant. The normalized values were computed using a proportional equation.

Results

Fourteen uptake experiments were completed between February and August 1977. Eight with the oyster *Crassostrea virginica*, five with the wedge clam *Rangia cuneata* and one with the clam *Macoma balthica*. In all but two of these, the animals were exposed to suspended contaminated sediments in flowing water. In the other two, oysters and *Rangia* were exposed to contaminated sediments by partial or total burial in an undisturbed bed in a tray.

Exposure periods consisted of approximately one to four weeks. Kepone concentrations in the sediment suspension were computed for each weekly period and for each of the progressively longer periods that represented the total duration of exposure.

Kepone levels in the sediment suspensions were classified as low, medium and high as labels of convenience. The mean hourly concentration for each weekly period in experiments where levels were classified as low ranged between 0.020 and 0.058 ppb (Tables 1-3). In experiments where levels were classified as medium and high, mean hourly concentrations ranged between 0.040 and 0.153 ppm.

Mean hourly concentrations for the total duration of exposure (one, two, three or four weeks) in experiments where levels were classified as low ranged between 0.027 and 0.058 ppb (Tables 4 and 5). In experiments where levels were classified as medium or high the range of mean hourly concentration was between 0.057 and 0.153 ppb.

Results are presented separately for each of the three bivalve species. No data are presented for the Kepone concentration in animals examined before the start of each experiment or for control animals because in every case they were under the level of detectability of the analytical procedure.

Crassostrea virginica

Figures 6-8 show the concentration of Kepone in oysters examined at weekly intervals after exposure to contaminated sediments in suspension in three series of experiments. The values in parentheses give the mean hourly concentration of Kepone in the sediments for the weekly period that immediately preceded removal for analysis of that particular sample of oysters.

Results of the first series of experiments showed a uniform progression in the concentration of Kepone in oysters with time (Figure 6). There was indication that an asymptotic level had been reached after two weeks. There also was a clear separation between the three lines which represented high, medium and low concentrations in sediments. A uniform progression was also evident in the second series of experiments although the absolute concentrations attained in oyster meats were lower than in the first series and there was no indication that an asymptotic level had been reached (Figure 7). In the third series there was neither a uniform progression nor suggestion of an asymptotic level.

The three sets of lines in Figures 6-8 did not appear to share a common pattern. However, they did show that the higher concentrations in oyster meats were associated with the higher concentrations in the sediments and vice versa. When the values for Kepone concentration in oyster meats in the three series of experiments (Tables 1-3) were grouped into three classes according to selected concentration ranges it was found that the values for Kepone in sediments also separated into three fairly distinguishable groups with different means. Eleven sediment values associated with concentrations in oyster meats between 0 and 0.10 ppm had a mean of 0.038 ppb (range: 0.020 - 0.098 ppb). Twelve values for concentration in sediment associated with concentrations in oyster meats between 0.101 and 0.199 had a mean of 0.058 ppb (range: 0.023 - 0.088 ppb). Five values for sediments associated with concentrations in oyster meats of 0.20 ppm or greater had a mean of 0.095 ppb (range: 0.070 - 0.113 ppb).

A plot of concentration of Kepone in oyster meats as a function of concentration in suspended sediments appears in Figure 9. Regression analysis showed a correlation between the two sets of data (correlation coefficient = 0.781).

Having obtained this correlation, the values for concentration in oyster meats were normalized on the basis of a constant, hourly concentration of Kepone in the sediments. The mean hourly concentration of Kepone in sediments for the whole duration of each experiment (approximately four weeks) was chosen as the normalization constant. The computed means appear in Table 4.

Plots of the normalized values for oyster meat concentrations appear in Figure 10 and 11. The marked dips in meat concentrations after two and three weeks of exposure during the third series of experiments have been eliminated in the normalized curves. The normalized curves suggest that an asymptotic level is reached after the first week of exposure in that series.

The curves for the first and second series were slightly altered by the conversion but the original trends shown were not appreciably changed. The curves for the first series still indicate an asymptotic plateau. Curves for the second series, on the other hand, still show a trend of increasing concentration in oyster meats with time. The high value seen for the third week in the borken line for the first period results from a relatively high value in the meats in the original data while the corresponding value in the suspended sediments was relatively low (medium concentration, Table 1).

There were significant differences in the temperatures at which the three series of experiments with oysters were conducted (Table 6). In the first series, York River water had to be heated to raise it to desirable levels. The minimum and maximum daily temperatures recorded near the source of our river water supply for each of the weekly periods included in the experiment were: 1st week, 3.2-7.6°C; 2nd week, 6.4-10.4°C; 3rd week, 9.0-12.8°C; and 4th week, 10.0-12.0°C. Water temperatures in the

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experimental trays ranged between 14.0 and 21.0°C during the four weeks included, with the average being between 17 and 18°C for each of the weekly periods.

The second and third series of experiments were conducted at ambient temperatures. These ranged between 18.3 and 25.7°C during the four weeks of the second series with an average for each week in the range of 20.9 to 23.5°C (Table 6). During the third series the overall range was 25.0 to 34.0°C with the weekly average ranging between 26.6 and 29.6°C.

During the first series of experiments, daily salinities ranged between 17.5 and 22.1‰ for the four weeks, and the weekly average ranged from 18.4 to 20.4‰ (Table 6). During the second series, the corresponding salinity ranges were 16.2 - 20.3‰ and 17.1-19.4‰. Likewise, the ranges of the corresponding averages for the third series were 20.2-23.6‰ and 20.6-23.1‰.

One of the experiments in the third series involved weekly analysis of Kepone concentration in the meats of oysters that had been held partially buried in an undisturbed bed of contaminated sediments. York River water flowing over the sediment bed was uncontaminated by Kepone. The concentration of Kepone in the sediments forming the bed averaged 1.77 ppm in two samples analyzed before the oysters were introduced (Table 7). A mixed sample from the same tray analyzed after the oysters were removed showed a concentration of 2.89 ppm. A sample collected from the top one centimeter layer of the tray after the oysters were removed had a Kepone concentration of 2.24 ppm.

After one week in the sediment bed the Kepone concentration in two samples of oysters averaged 0.037 ppm (Table 7). The concentration in oyster meats decreased gradually during the next three weeks below the detectability level of the analytical techniques, *i.e.*, 0.02 ppm.

Mean sizes of oysters used in the three experiments appear in Table 9. They ranged between 7 and 8 cm in height during the first and third series of experiments and between 5 and 6 cm in the second series.

Oyster Biodeposits

Oysters concentrated Kepone in their biodeposits to levels thousands of times higher than those found in the suspended sediments (Table 8). The concentration factors for feces ranged from 11,000 to 55,000. In pseudofeces, the range was between 3,000 to 20,000. The concentration in feces was always higher than that in pseudofeces but the magnitude of the difference varied considerably between the paired sampled compared.

Concentration of Kepone in sediments that settled by gravity in the tray compartments was usually slightly higher than those in pseudofeces. However, it was also significantly lower than that in feces.

Rangia cuneata

Five experiments were conducted with the wedge clam *Rangia cuneata* during the second and third series of experiments. In four, animals were exposed to contaminated sediments in suspension and in one they were buried in a bed of contaminated sediments.

The results obtained for *Rangia* during the second series of experiments are almost identical to those obtained for oysters during the same series (Table 2, Figures 12 and 7). Most of the actual values found at any one weekly interval were close and the line trends are similar.

The data for Rangia in the thrid series of experiments were somewhat different from those for oysters (Table 3, Figures 13 and 8). Distribution of the weekly values for Rangia meats tended to remain at approximately the same level after the first week with a slight dip in the third week samples. The oyster data showed a greater vertical displacement of the weekly values. The data for both animals showed a fairly distinct separation between the lines for low and high Kepone concentrations in the sediments.

Rangia buried in undisturbed contaminated sediments accumulated Kepone to low levels (Table 7, Figure 13). After the first week high of 0.05 ppm there was a gradual decrease with time to 0.03 ppm after four weeks. Rangia receiving low concentrations of Kepone in suspension accumulated slightly more Kepone than those buried in the sediments even though the latter had a Kepone concentration several thousand times greater (2 ppm in the bed sediments vs. 0.02 to 0.06 ppb in the water column).

Water temperatures in the trays holding Rangia during the second series of experiments were slightly lower than during the third series (Table 6). The range during the second series was between 18 and 20°C and during the third series it was between 20 and 22°C. There was substantially no difference in water salinities during the two series.

Mean sizes and Rangia used in these experiments appear in Table 10. They ranged between 4 and 5 cm in height.

Macoma balthica

A single experiment was conducted with the clam Macoma balthica during the second series. The Macoma were held in the same tray with oysters receiving sediments in suspension at a high concentration of Kepone. However, they were placed in the tray one week later than the oysters and consequently, they remained in the tray one week after all the oysters had been removed.

The Macoma laid directly on the bottom of the tray and, being fairly small (average height was between 1.4 and 1.7 cm; Table 11) were in close contact with the contaminated sediments that settled on the tray bottom. Sediments settling to the bottom of the experimental trays were removed every two or three days.

The Macoma accumulated Kepone at the fastest rate of the three species studied to date. After three weeks the concentration was 0.33 ppm (Figure 14). During the fourth week there was a slight drop to 0.30 ppm.

Mean water temperatures in the trays holding Macoma ranged between 21 and 24°C during the four weekly periods (Table 6). Mean water salinities ranged between 17 and 20‰.

Mean sizes of Macoma used in these experiments appear in Table 11. They ranged around 1.5 cm in height.

Condition index. Measurements of the meat quality of samples of the experimental animals showed no significant differences between those analyzed at the start of the experiments and those analyzed after approximately four weeks in the experimental trays.

Discussion

The bivalves Crassostrea virginica, Rangia cuneata and Macoma balthica concentrated Kepone from suspended sediments by factors ranging between 1000 and 3000 over that in the water column.

There was little difference in the results obtained for Crassostrea and Rangia. Macoma, however, accumulated Kepone in greater concentrations than the other two species.

Crassostrea and Rangia showed similar trends in uptake of Kepone from suspension. This showed that the two species have similar feeding habits. As suspension feeders, they are reacting in a similar manner to the presence of the sediments in suspension. Such a similarity was reinforced by the experiments in which individuals of the two species were buried partly or fully in a bed of contaminated sediments. Neither one of the two species accumulated much Kepone under those circumstances. Water flow over the sediment beds was relatively slow and the water-sediment interface was not disturbed. Therefore, very little of the sediment was re-suspended. Concentrations in Rangia were slightly higher than those for oysters and if there is any significance to the difference it may be an indication that by being fully buried with its siphon close to the sediment surface, Rangia had access to sediments not available to oysters.

The data for oysters showed a strong correlation between the mean hourly concentration of Kepone in suspended sediments, computed for weekly intervals, and the mean concentration in oyster samples exposed to those sediments during the same weekly period. As illustrated in Figures 6-8, usually the Kepone in oyster meats decreased or increased from one week to the next following a decrease or increase in Kepone in the sediments during the intervening week. The validity of such a correlation is further reinforced by the similarity between the patterns of the curve for low and high sediment concentrations in each of the three series of experiments.

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A weaker correlation (0.614) was also found in the data for Rangia. Further collection of data for Macoma will be necessary before it can be determined if the relationship holds for that species.

This correlation indicates that, at the temperatures included, oysters and possibly other bivalves such as Rangia and Macoma depurate themselves of Kepone continuously at the same time that they ingest and accumulate it. Therefore, in order for the Kepone level to remain at a high level, the Kepone concentration in suspension will also have to remain at a correspondingly high level.

Consequently, disturbance of river bottoms contaminated with Kepone by natural processes or other processes initiated by man, which would result in an increase in the suspended sediment load, appear to be capable of causing a sharp increase in the levels of Kepone in individuals of bivalve populations within reach of the increased load. On the other hand, it would appear that such an increase in Kepone in the affected animals would also decrease sharply once the disturbance is terminated.

It is difficult to evaluate with the data obtained to date the influence of temperature on the uptake and depuration of Kepone by oysters and Rangia. More data are required to establish that.

Further studies are planned to investigate this relationship between Kepone in sediments and in bivalves. The effect of concentrations in the sediments higher than those tested so far will be considered. The effect of higher water flows capable of

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causing suspension of surface sediments in a bed holding buried animals will also be studied. Experiments that include combinations of contamination and depuration of bivalves will also be conducted.

The levels of Kepone flowing over animals in experimental trays have been fairly low - never higher than 0.15 ppb in the water column - in the experiments conducted so far. This has been dictated by restrictions in the capability of our system and personnel to maintain larger quantities of sediments in stock suspensions and flowing over the animals around the clock for four weeks. Changes required to achieve higher sediment concentrations will be implemented in the forthcoming series of experiments.

The data indicate that a leveling in the concentration of Kepone in oysters and Rangia occurs after the first week of exposure. This was seen best in the curves obtained by normalization of the data using as a constant the mean hourly concentration of Kepone in the sediments for the duration of each experiment. Since no animal samples were analyzed for a period shorter than one week it is quite possible that the leveling may occur sooner than one week. Either way, this is another indication of the efficiency of these bivalves to depurate themselves of Kepone since it is evidently a balance between uptake and depuration that is responsible for the leveling off in the curves.

Analysis of oyster biodeposits indicated that Kepone is concentrated in feces to levels many thousand times higher than it is present in the water column. These observations re-emphasize the importance of the effect biodeposition can have on the physico-chemical characteristics of sediments. At the same time oysters accumulate Kepone in their tissues to levels up to 3000 times that in the water column, they are also re-depositing high concentrations of the chemical on the bottom. This re-deposition is being done in the form of material less likely to be resuspended because of its nature as an aggregate.

Kepone concentration in oyster pseudofeces was not much different than that found in sediments that settled by gravity onto the tray bottom. Therefore, there appears to be no indication that pseudofeces contribute to the deposition of Kepone-rich sediments any more than natural sedimentation would. However, pseudofeces form an aggregate which like feces may also resist re-suspension to a greater extent than naturally-settling sediments.

There is no way to establish to what extent sediments settling by gravity in experimental trays are included in the samples of feces and pseudofeces collected. However, the concentrations recorded for feces are so much greater than in the natural sediments and the bulk of the feces was so obviously greater than the fine blanket of sediments on the bottom of the tray, that it can be safely infered that their contribution to the values recorded for feces are minimal.

Literature Cited

Haven, D. S. 1960. Seasonal cycle of condition index of oysters in the York and Rappahannock Rivers. Proc. Nat'l Shellfish Assoc. 54: 42-65.

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Table 1. Concentration of Kepone in sediments and in the meats of oysters during successive exposure periods in first series of Kepone uptake experiments. 24 February - 27 March, 1977

Exposure Period	No. days	Sediments (ppb) Range	Sediments (ppb) Hourly Mean	Meats Mean (ppm)	Concentration Factor
Low Sediment Concentration					
1	6.9	0.014 - 0.039[1]	0.027	0.086	3185
2	14.8	0.014 - 0.066	0.037	0.125	3289
3	21.8	0.003 - 0.045	0.023	0.135	5625
4	29.2	0.015 - 0.046	0.033	0.113	3228
Medium Sediment Concentration					
1	6.9	0.027 - 0.083	0.057	0.130	2281
2	14.8	0.027 - 0.142	0.073	0.160	2078
3	21.8	0.006 - 0.091	0.045	0.185	3854
4	29.2	0.029 - 0.092	0.067	0.133	1900
High Sediment Concentration					
1	6.9	0.040 - 0.197	0.082	0.185	2256
2	14.8	0.054 - 0.197	0.104	0.250	2294
3	21.8	0.008 - 0.133	0.070	0.210	2838
4	29.2	0.044 - 0.137	0.098	0.257	2495

[1] Short period of time when no contaminated sediments were being added to the water flowing over the animals (i.e., sediment concentration = 0) are not included in range. However, they were used in computing the mean. This includes the final 8-9 hours when animals were allowed to flush out sediments in their digestive tract prior to removal for analysis.

Table 2. Concentration of Kepone in sediments and in animal meats during successive exposure periods in second series of Kepone uptake experiments. 13 May - 19 June, 1977.

Exposure Period	No. Days	Sediments (ppb) Range	Sediments (ppb) Hourly mean	Meats Mean (ppm)	Concentration Factor
Low Concentration					
Oysters:					
1	7.3	0.024 - 0.078[1]	0.042	0.039	931
2	14.8	0.024 - 0.058	0.035	0.058	1667
3	22.0	0.017 - 0.040	0.026	0.064	2424
4	29.0	0.028 - 0.055	0.038	0.096	2526
Rangia:					
1	7.3	0.024 - 0.077	0.039	0.025	641
2	14.8	0.024 - 0.057	0.034	0.050	1453
3	22.0	0.016 - 0.039	0.025	0.048	1912
4	29.0	0.028 - 0.054	0.037	0.083	2237
High Concentration					
Oysters:					
1	7.2	0.054 - 0.178	0.098	0.09	905
2	14.7	0.058 - 0.139	0.086	0.16	1860
3	21.9	0.040 - 0.095	0.063	0.11	1732
4	28.9	0.068 - 0.132	0.093	0.23	2484
Rangia:					
1	7.2	0.057 - 0.188	0.104	0.05	521
2	14.7	0.061 - 0.147	0.091	0.14	1545
3	21.9	0.043 - 0.100	0.067	0.11	1644
4	28.9	0.071 - 0.140	0.098	0.22	2254
Macoma:					
1	7.5	0.058 - 0.139	0.086	0.13	1512
2	14.7	0.040 - 0.095	0.063	0.19	2992
3	21.7	0.068 - 0.132	0.093	0.33	3564
4	29.0	0.095 - 0.131	0.098	0.30	3067

[1] Short periods of time when no contaminated sediments were being added to the water flowing over the animals (i.e., sediment concentration = 0 are not included in range. However, they were used in computing the mean. This includes the final 8-9 hours when arrivals were allowed to flush out sediments in their digestive tracts prior to removal for analysis.

Table 3. Concentration of Kepone in sediments and in the meats of oysters and Rangia during successive exposure periods in third series of Kepone uptake experiments. 8 July - 9 August, 1977.

Exposure Period	No. Days	Sediments (ppb) Range	Sediments (ppb) Hourly mean	Meats Mean (ppm)	Concentration Factor
Low Sediment Concentration					
Oysters:					
1	8.0	0.018 - 0.087[1]	0.047	0.113	2404
2	15.4	0.012 - 0.058	0.020	0.067	3350
3	23.4	0.007 - 0.041	0.020	0.049	2450
4	31.0	0.008 - 0.085	0.035	0.067	2030
Rangia:					
1	8.0	0.020 - 0.097	0.058	0.058	1000
2	15.4	0.014 - 0.066	0.026	0.063	2423
3	23.4	0.008 - 0.044	0.024	0.041	1708
4	31.0	0.008 - 0.082	0.041	0.068	1658
High Sediment Concentration					
Oysters:					
1	8.1	0.046 - 0.223	0.113	0.21	1858
2	15.5	0.031 - 0.096	0.043	0.10	2325
3	23.5	0.019 - 0.078	0.040	0.069	1725
4	31.0	0.019 - 0.195	0.088	0.16	1818
Rangia:					
1	8.1	0.058 - 0.284	0.153	0.12	784
2	15.5	0.039 - 0.121	0.065	0.12	1846
3	23.5	0.021 - 0.086	0.053	0.085	1604
4	31.0	0.023 - 0.230	0.126	0.125	992

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[1] Short periods of time when no contaminated sediments were being added to the water flowing over the animals (i.e., sediment concentration = 0) are not included in range. However, they were used in computing the mean. This includes the final 8-9 hours when animals were allowed to flush out sediments in their digestive tract prior to removal for analysis.

Table 4. Normalized values for Kepone concentration in oysters exposed in laboratory trays to suspensions of sediments contaminated with Kepone. Presented as a function of the mean hourly concentration in sediments for the duration of each experiment.

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Exposure Period	Length of Exposure (days)	Mean hourly conc. Kepone for each period (ppb)	Mean hourly conc. Kepone for accumulated time periods (ppb)	Actual conc. Kepone in oyster meats[1] (ppm)	Normalized conc. Kepone in oyster meats[2] (ppm)
First series of experiments (24 Feb - 27 March 1977)					
1	6.9	0.027	0.027	0.087	0.097
2	14.8	0.037	0.032	0.125	0.101
3	21.8	0.023	0.029	0.136	0.177
4	29.2	0.033	0.030[3]	0.113	0.103
1	6.9	0.057	0.057	0.130	0.139
2	14.8	0.073	0.066	0.160	0.134
3	21.8	0.045	0.059	0.188	0.255
4	29.2	0.067	0.061[3]	0.133	0.121
1	6.9	0.082	0.082	0.185	0.203
2	14.8	0.104	0.094	0.250	0.216
3	21.8	0.070	0.085	0.209	0.269
4	29.2	0.098	0.090[3]	0.257	0.236
Second series of experiments (13 May - 11 June 1977)					
1	7.3	0.042	0.042	0.039	0.032
2	14.8	0.035	0.038	0.058	0.058
3	22.0	0.026	0.034	0.064	0.086
4	29.0	0.038	0.035[3]	0.096	0.088
1	7.2	0.098	0.098	0.090	0.078
2	14.7	0.086	0.092	0.160	0.158
3	21.9	0.063	0.083	0.110	0.148
4	28.9	0.093	0.085[3]	0.230	0.210

Table 4, (con'td)
Normalized values in oyster meats

Third series of experiments (8 July - 9 Aug. 1977)

Exposure Period	Length of Exposure (days)	Mean hourly conc. Kepone for each period (ppb)	Mean hourly conc. Kepone for accumulated time periods (ppb)	Actual conc. Kepone in oyster meats[1] (ppm)	Normalized conc. Kepone in oyster meats[2] (ppm)
1	8.0	0.047	0.047	0.110	0.072
2	15.4	0.020	0.034	0.067	0.104
3	23.4	0.020	0.029	0.049	0.076
4	31.0	0.035	0.031[3]	0.067	0.059
1	8.1	0.113	0.113	0.210	0.133
2	15.5	0.043	0.080	0.100	0.167
3	23.5	0.040	0.066	0.069	0.124
4	31.0	0.088	0.072[3]	0.160	0.131

[1] Determined analytically

[2] Normalized value computed proportionally

[3] Mean value reference used in computing normalized values in oysters

Table 5. Mean hourly concentration of Kepone in sediment suspensions flowing over *Rangia* and *Macoma* during the total duration of each period of exposure in experimental trays.

Species	Total duration of exposure (days)	Mean hourly concentration for each weekly period (ppb)	Mean hourly concentration for full period (ppb)
Rangia:	Second series of experiments (13 May - 11 June 1977)		
	Low sediment concentration		
	7.3	0.039	0.039
	14.8	0.034	0.037
	22.0	0.025	0.033
	29.0	0.037	0.034
	High sediment concentration		
	7.2	0.104	0.104
	14.7	0.091	0.097
	21.9	0.067	0.087
	28.9	0.098	0.090
	Third series of experiments (8 July - 9 August)		
	Low sediment concentration		
	8.0	0.058	0.058
	15.4	0.026	0.043
	23.4	0.024	0.036
	31.0	0.041	0.037
	High sediment concentration		
	8.1	0.153	0.153
	15.5	0.065	0.111
	23.5	0.053	0.091
	31.0	0.126	0.100

Table 5, Continued

Species	Total duration of exposure (days)	Mean hourly concentration for each weekly period (ppb)	Mean hourly concentration for full period (ppb)
Macoma:	Second series of experiments (8 July - 9 August 1977)		
	High sediment concentration		
	7.5	0.086	0.036
	14.7	0.063	0.075
	21.7	0.093	0.081
	29.0	0.098	0.085

Table 6. Range and mean of water temperature and salinity in trays holding animals during Kepone uptake experiments.

	Weekly Period	Temperature (C)		Salinity (o/oo)	
		Range	Mean	Range	Mean
1st Series (Feb. 24 - March 27, 1977)					
Oysters:					
	1st	14.0 - 20.8	17.2	19.3 - 22.1	20.4
	2nd	15.0 - 21.0	17.7	19.1 - 20.6	20.2
	3rd	16.1 - 20.8	18.5	19.1 - 20.1	19.7
	4th	14.8 - 19.6	17.0	17.5 - 19.2	18.4
2nd Series (May 13 - June 19, 1977)					
Oysters:					
	1st	18.3 - 25.0	20.9	17.5 - 19.2	18.3
	2nd	21.3 - 25.0	22.4	16.2 - 17.9	17.1
	3rd	22.3 - 25.7	23.5	17.5 - 19.5	18.3
	4th	20.5 - 25.0	21.5	18.9 - 20.3	19.4
Macoma:					
	1st	21.3 - 25.0	22.4	16.2 - 17.9	17.1
	2nd	22.3 - 25.7	23.5	17.5 - 19.5	18.3
	3rd	20.5 - 25.0	21.5	18.9 - 20.3	19.4
	4th	20.7 - 25.9	23.7	19.9 - 20.0	19.9
Rangia:					
	1st	16.6 - 21.2	18.6	0.5 - 7.3	5.5
	2nd	18.7 - 20.8	19.5	5.0 - 6.4	5.4
	3rd	19.0 - 22.3	20.4	1.3 - 7.9	5.1
	4th	18.0 - 21.3	19.2	3.2 - 6.4	5.0
3rd Series (July 8 - August 9, 1977)					
Oysters:					
	1st	26.9 - 34.0	29.6	20.2 - 20.8	20.6
	2nd	26.8 - 32.0	29.3	20.9 - 22.1	21.6
	3rd	25.0 - 30.0	26.6	21.9 - 22.9	22.5
	4th	26.5 - 30.9	28.5	22.9 - 23.6	23.1
Rangia:	1st	20.5 - 24.3	22.9	2.8 - 8.7	5.9
	2nd	20.4 - 24.9	22.5	3.9 - 8.8	6.1
	3rd	19.0 - 22.0	20.3	4.2 - 6.0	5.4
	4th	20.0 - 23.2	21.4	2.3 - 6.8	5.4

Table 7. Concentration of Kepone in the meats of oysters and Rangia held in control trays receiving no contaminated sediments and in test trays partially or fully buried in unsieved sediments contaminated with Kepone. July 8 - August 9, 1977. Means in parentheses.

	Exposure Period	Cumulative No. Days	Kepone Conc. in Animals Buried in Sediments (ppm)	Kepone Conc. in Control Animals (ppm)
A.	Oysters (partially buried in test trays):			
	1	8.5	0.034 0.040 (0.037)	≤0.007
	2	15.9	0.024	≤0.009
	3	23.9	0.014 0.018 (0.016)	≤0.005
	4	31.6	0.014 ≤0.009 (≤0.007)	≤0.004
	Rangia (fully buried in mud)			
	1	8.5	0.067 0.035 (0.051)	0.011
	2	15.9	0.053 0.039 (0.046)	≤0.006
	3	23.9	0.029 0.038 (0.033)	≤0.003
	4	31.6	0.034 0.031 (0.032)	≤0.007

Table 7 (Continued)

B. Concentration of Kepone (in ppm) in unsieved sediments used in test trays in which animals were fully or partially buried.

1. Mixed samples at start of experiment: (Same sediments used in both trays)	0.71 2.83 (1.77)
2. Fractionated and mixed samples at end of experiment:	
a. Mixed sample from oyster trays	2.89
b. Sample from top 1-cm layer in oyster tray	2.24
c. Mixed sample from *Rangia* tray	2.12
d. Sample from top 1-cm layer in *Rangia* tray	0.64

Table 8

Concentration of Kepone in oyster biodeposits and in sediments settling out by gravity in same tray holding the oysters.

Log Book and Page No.	Date Collected 1977	No. Days of Accumulation	Mean Hourly Concentration in Suspended Sediments (ppb)	Feces (ppm)	Feces Concentration Factor	Pseudo-feces (ppm)	Pseudofeces Concentration Factor	Gravity-Settling Sediments (ppm)	Gravity-Settling Sediments Concentration Factor
HK1-16	22 March	6	--	1.59		0.018			
HK1-23	4 April	5	--	0.33		0.13		0.13	
HK1-52	15 July	7	0.047	Lost		0.36	(7,659)	0.51	(10,851)
	15 July	7	0.113	1.30	(11,504)	0.34	(3,008)	0.41	(3,628)
HK1-56	23 July	7	0.20	0.80	(40,000)	0.40	(20,000)	0.52	(26,000)
	23 July	7	0.043	0.76	(17,674)	0.60	(13,953)	0.65	(15,116)
HK1-60	31 July	6	0.020	0.79	(39,500)	0.33	(16,500)	0.47	(23,500)
	31 July	6	0.040	1.23	(30,750)	0.29	(7,250)	0.48	(12,000)
HK1-64	9 August	7	0.033	1.83	(55,454)	0.57	(17,272)	0.23	(6,969)
	9 August	7	0.088	1.83	(20,795)	0.30	(3,409)	0.37	(4,204)

Table 9. Mean height (in cm) of oysters in different samples analyzed for Kepone during uptake experiments. Number of animals in each sample appears in parentheses.

Exposure Period	Low Kepone conc. in sediments	Medium Kepone conc. in sediments	High Kepone conc. in sediments	Animals Buried in mud	Control Animals
First series of experiments (24 Feb - 27 March 1977)					
1	(4) 6.7	(4) 7.2	(4) 6.1		(4) 7.8
	(3) 7.8	(3) 7.1	(3) 7.0		(3) 7.3
2	(4) 7.7	(4) 7.6	(4) 7.1		(4) 7.1
	(3) 7.4	(3) 7.5	(3) 7.0		(3) 7.7
3	(4) 7.2	(4) 7.3	(4) 6.7		(4) 7.6
	(3) 7.0	(3) 7.1	(3) 6.6		(3) 7.3
4	(4) 7.1	(4) 6.1	(4) 7.8		(4) 7.8
	(3) 7.2	(4) 7.3	(4) 7.8		(4) 8.4
	(4) 7.8	(5) 7.3	(4) 7.4		(3) 7.5
Second series of experiments (13 May - 19 June 1977)					
1	(8) 5.8		(8) 5.7		
2	(4) 6.0		(4) 5.6		(2) 7.9
	(4) 5.4		(4) 4.3		(4) 6.0
3	(3) 6.9		(3) 6.4		(4) 6.3
	(5) 5.4		(5) 4.8		(4) 4.9
4	(4) 5.7		(6) 5.1		(3) 6.6
	(4) 5.1		(5) 5.5		(5) 5.4
	(5) 5.6				
Third Series of experiments (8 July - 9 Aug., 1977)					
1	(3) 8.1		(3) 7.2	(3) 6.6	(4) 7.5
	(2) 7.7		(2) 7.9	(3) 7.2	
2	(3) 7.9		(3) 7.6	(3) 6.1	(4) 7.7
	(3) 7.6		(3) 7.6	(3) 7.4	

Table 9, Cont'd)

Exposure Period	Low Kepone conc. in sediments	Medium Kepone conc. in sediments	High Kepone conc. in sediments	Animals Buried in mud	Control Animals
3	(3) 7.6		(3) 7.5	(3) 6.9	(4) 7.7
	(3) 7.5		(3) 7.0	(3) 7.3	
4	(4) 7.1		(3) 7.7	(4) 7.0	(3) 7.7
	(4) 6.8		(4) 6.3	(3) 7.4	(3) 8.2

Table 10. Mean height (in cm) of Rangia in different samples analyzed for Kepone during uptake experiments. Number of animals in each sample appears in parentheses.

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Exposure period	Low Kepone conc. in sediments	High Kepone conc. in sediments	Animals buried in mud	Control Animals
Second series of experiments (13 May - 19 June 1977)				
1	(8) 4.9	(8) 4.6		(8) 4.8
2	(4) 4.9 (4) 4.9	(4) 4.8 (4) 4.8		(4) 5.0 (4) 4.8
3	(4) 4.7 (4) 4.7	(4) 4.7 (4) 4.8		(4) 4.7 (4) 4.8
4	(8) 4.6 (8) 4.7 (8) 4.8	(8) 4.7 (8) 4.7 (8) 4.6		(8) 4.5 (7) 4.7
Third series of experiments (8 July - 9 Aug. 1977)				
1	(4) 5.01	(2) 5.31 (3) 4.90	(3) 4.85 (3) 5.04	(5) 5.20
2	(4) 4.99 (4) 4.49	(4) 4.88 (4) 4.92	(4) 4.92 (3) 5.02	(6) 4.74
3	(4) 5.00 (4) 5.15	(5) 5.02 (4) 4.89	(4) 5.12 (4) 4.96	(6) 4.98
4	(4) 5.03 (5) 4.73	(5) 4.83 (6) 4.79	(5) 5.00 (5) 5.24	(5) 4.88 (5) 4.75

Table 11. Mean height (in cm) of *Macoma* in different samples analyzed for Kepone during uptake experiments. Number of animals in each sample appears in parentheses.

Exposure Period	High Kepone conc. in sediments	Control Animals
Second series of experiments (13 May - 19 June 1977)		
1	(15) 1.7	(10) 1.6
2	(12) 1.6	(10) 1.6
3	(12) 1.5	(11) 1.6
4	(10) 1.4	(7) 1.6

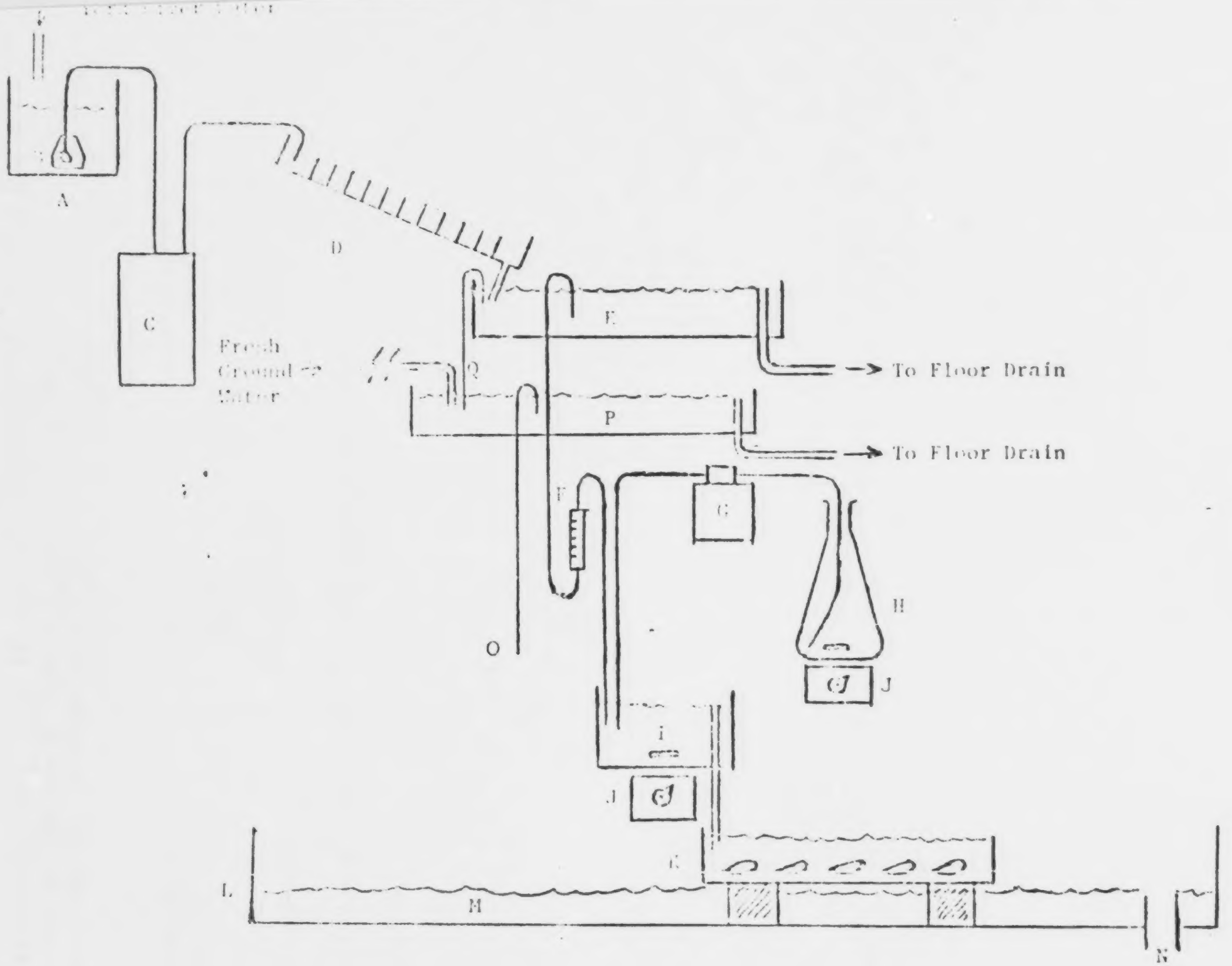
A
C
D
Fresh
Ground-Water
Q
E
P
To Floor Drain
To Floor Drain
F
G
H
O
I
J
J
K
L
M
N

Figure 1. Set-up of apparatus used in uptake experiments with bivalve molluscs in three series of experiments. Identification of individual components appears on next page.

Key to identification of components in Figure 1

A. Constantly-overflowing box providing York River water supply to system.

B. Submersible pump.

C. Heat exchanger system.

D. Cascading trough used to allow escape of gases coming out of suspension as result of river water being heated up.

E. Constantly-overflowing overhead trough from which water for experimental trays was siphoned.

F. Flow meter.

G. Peristaltic pump used to meter out sediment suspension.

H. Flask holding sediment suspension.

I. Mixing chamber receiving simultaneously York River water and sediment suspension.

J. Magnetic stirrer.

K. Experimental tray holding oysters.

L. Wet table holding experimental trays.

M. Drain pipe maintained a water level of about one-inch on wet table. This served as first component of a series of sediment trays.

N. Water from wet table overflowed into a series of three other sediment traps.

O. Siphon to mixing chamber of Rangia trays.

P. Constantly-flowing overhead trough from which water of low salintiy for experimental trays was siphoned.

Q. Siphon used to add river water from Trough E to fresh water in Tray P.

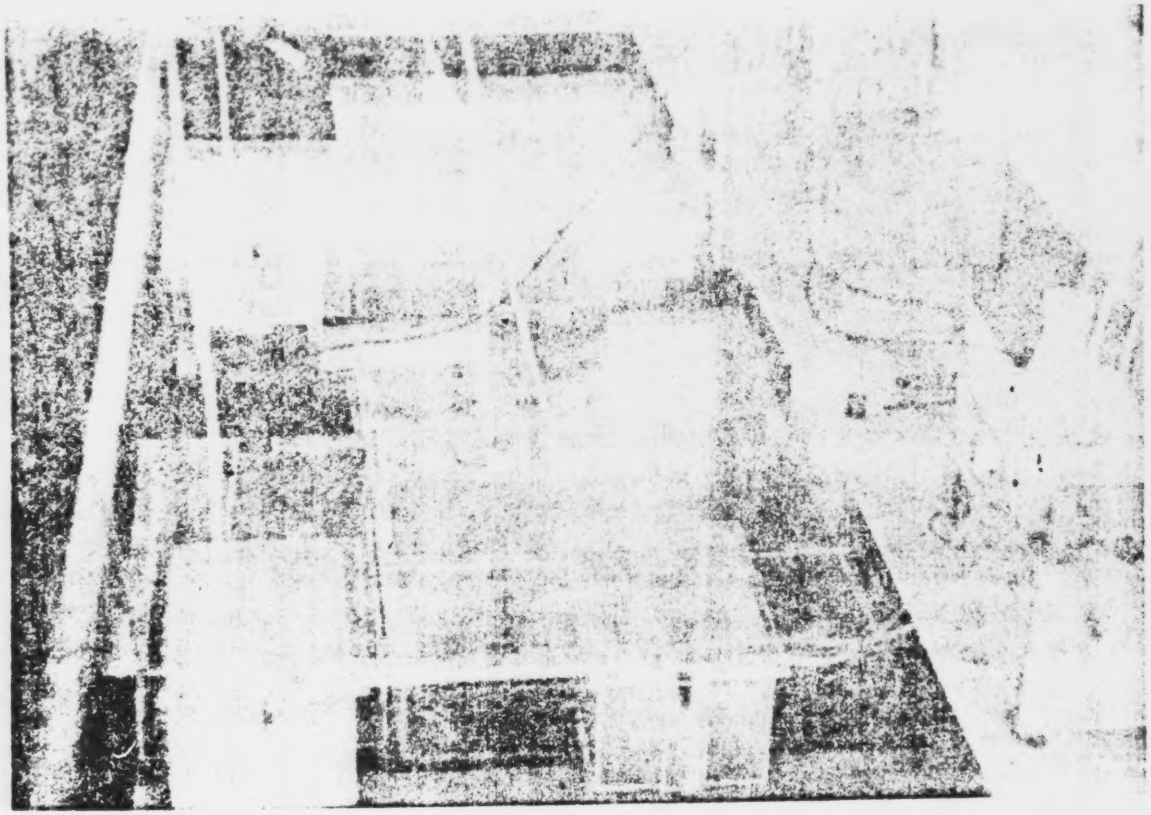

Figure 2. Arrangement of trays, mixing chambers and peristaltic pumps in third series of experiments in which animals received contaminated sediments in suspension. Oysters in large trays and *Rangia* in small ones.

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Figure 3. Control oysters (A) and Rangia (B) in small trays at start of third series of experiments.

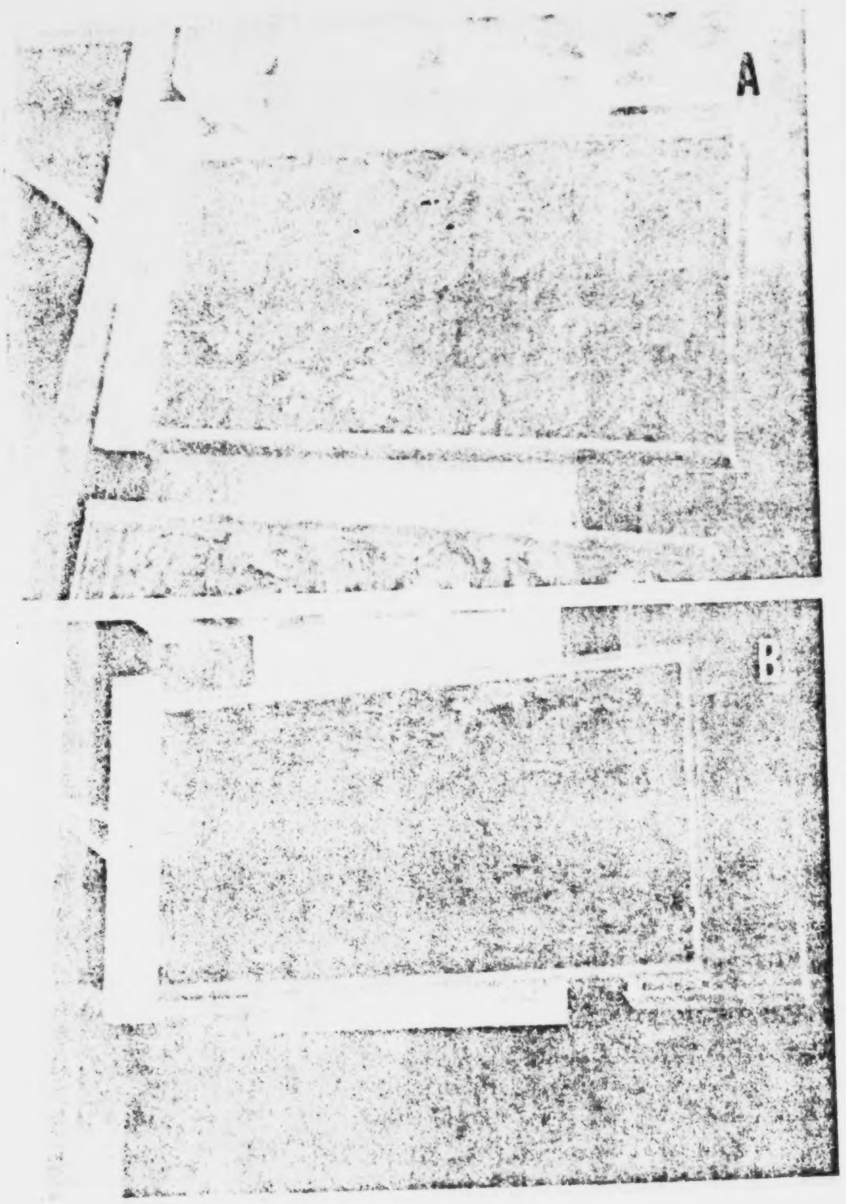
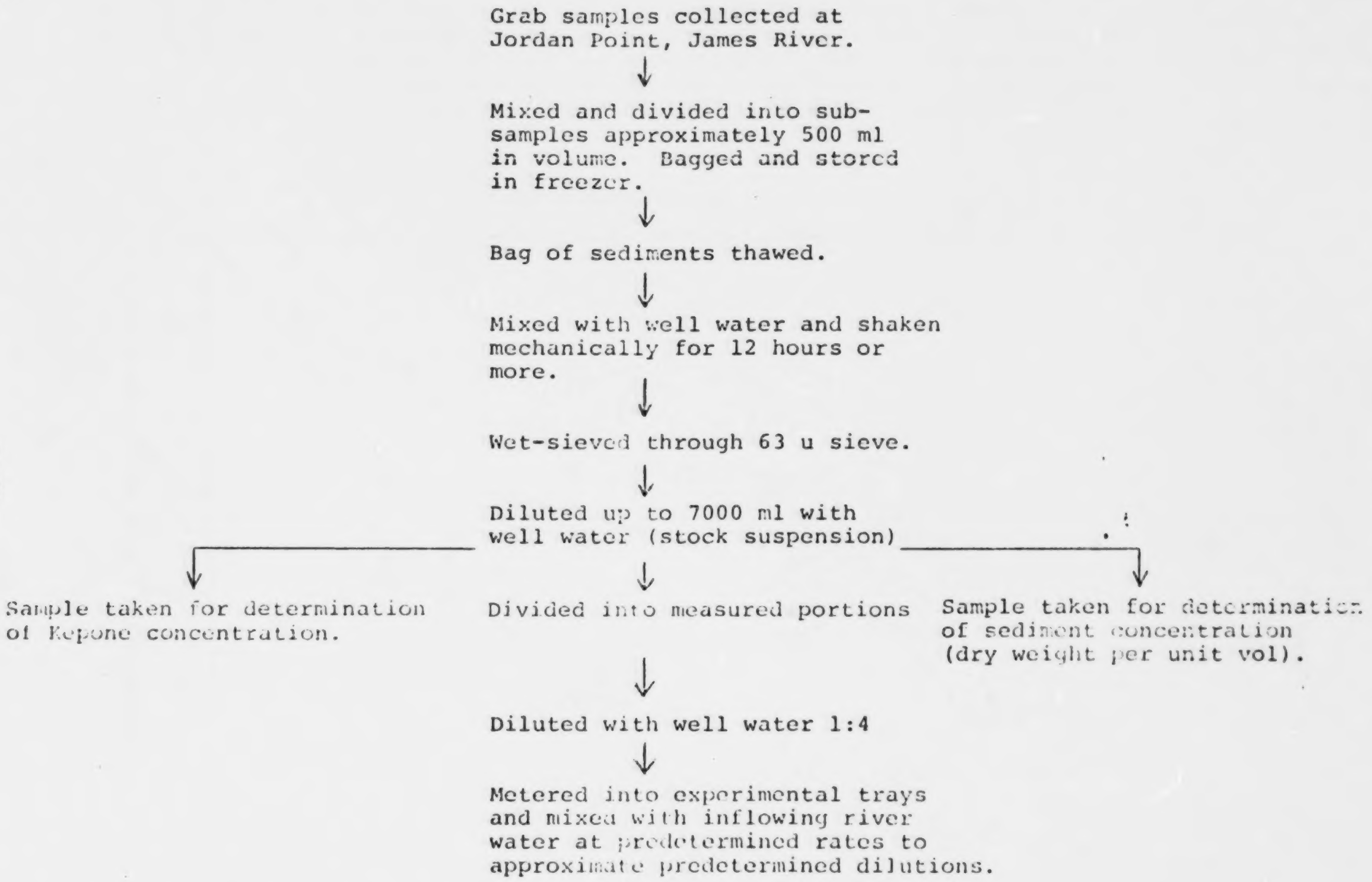


Figure 4. Oysters (A) and Rangia (B) partially buried in bed of sediments contaminated with Kepone at start of third series of experiments. Subsequently Rangia buried themselves fully.



Grab samples collected at Jordan Point, James River.

Mixed and divided into subsamples approximately 500 ml in volume. Bagged and stored in freezer.

Bag of sediments thawed.

Mixed with well water and shaken mechanically for 12 hours or more.

Wet-sieved through 63 u sieve.

Diluted up to 7000 ml with well water (stock suspension)

Sample taken for determination of Kepone concentration.

Divided into measured portions

Sample taken for determination of sediment concentration (dry weight per unit vol).

Diluted with well water 1:4

Metered into experimental trays and mixed with inflowing river water at predetermined rates to approximate predetermined dilutions.

Figure 5. Flow chart showing steps taken in preparation of sediments contaminated with Kepone for introduction into trays holding experimental animals.

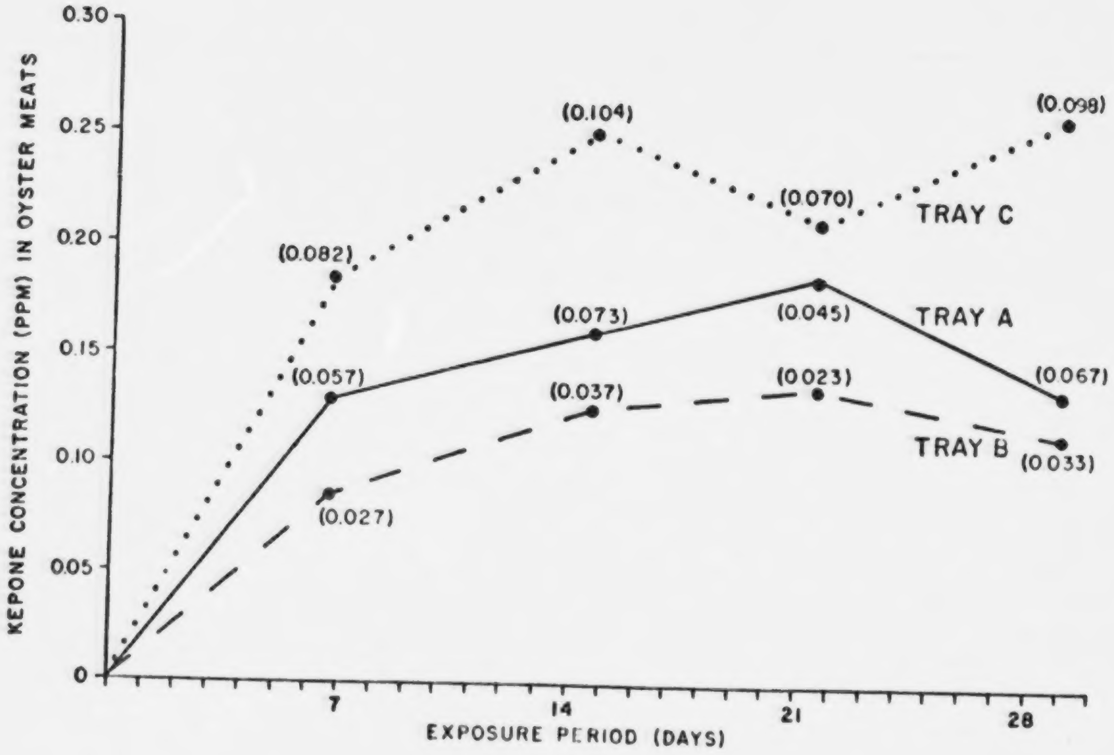


Figure 6. Mean concentration of Kepone in meats of oysters exposed to contaminated sediments in suspension. First series of experiments, 24 Feb.-27 March 1977. Figures in parentheses are mean hourly concentration of Kepone in sediments for weekly period ending at that point.

438

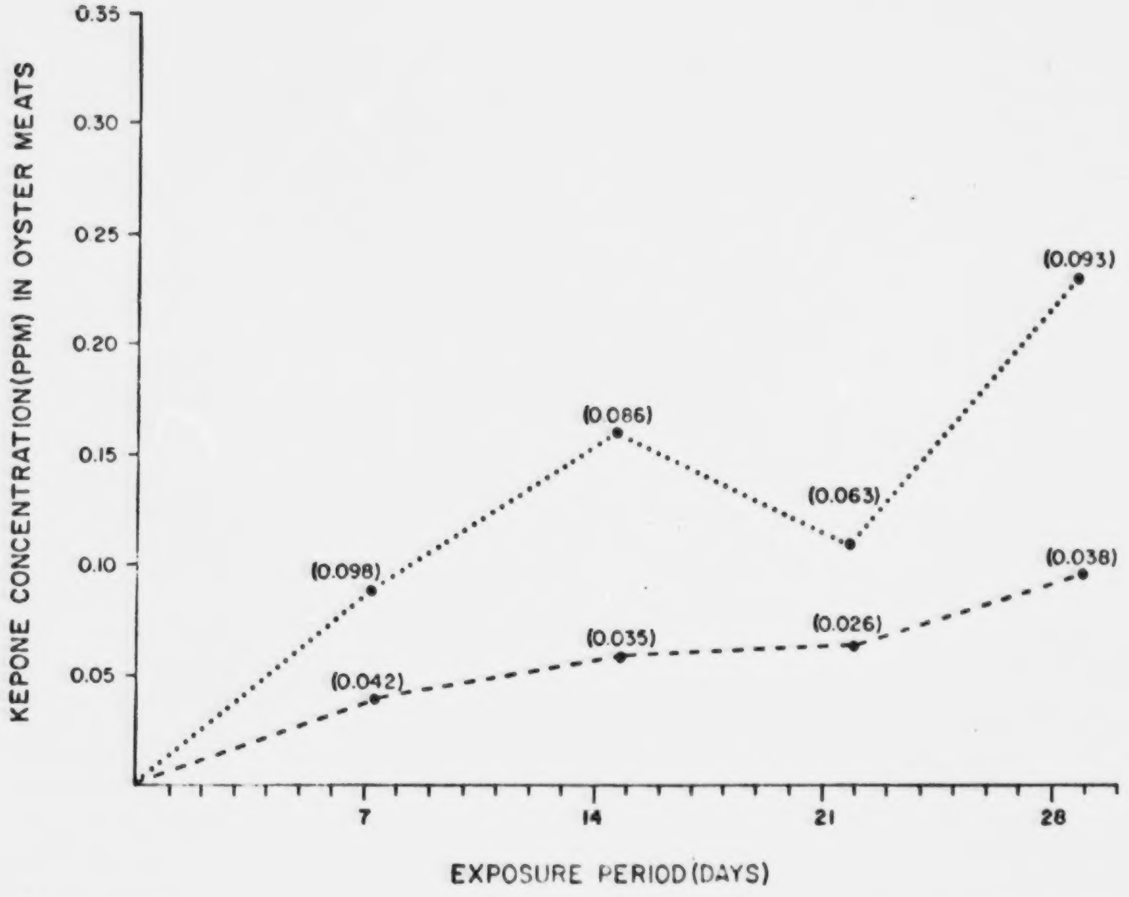


Figure 7. Mean concentration of Kepone in meats of oysters exposed to contaminated sediments in suspension. Second series of experiments, 13 May-11 June 1977. Figures in parentheses are mean hourly concentration of Kepone in sediments for weekly period ending at that point.

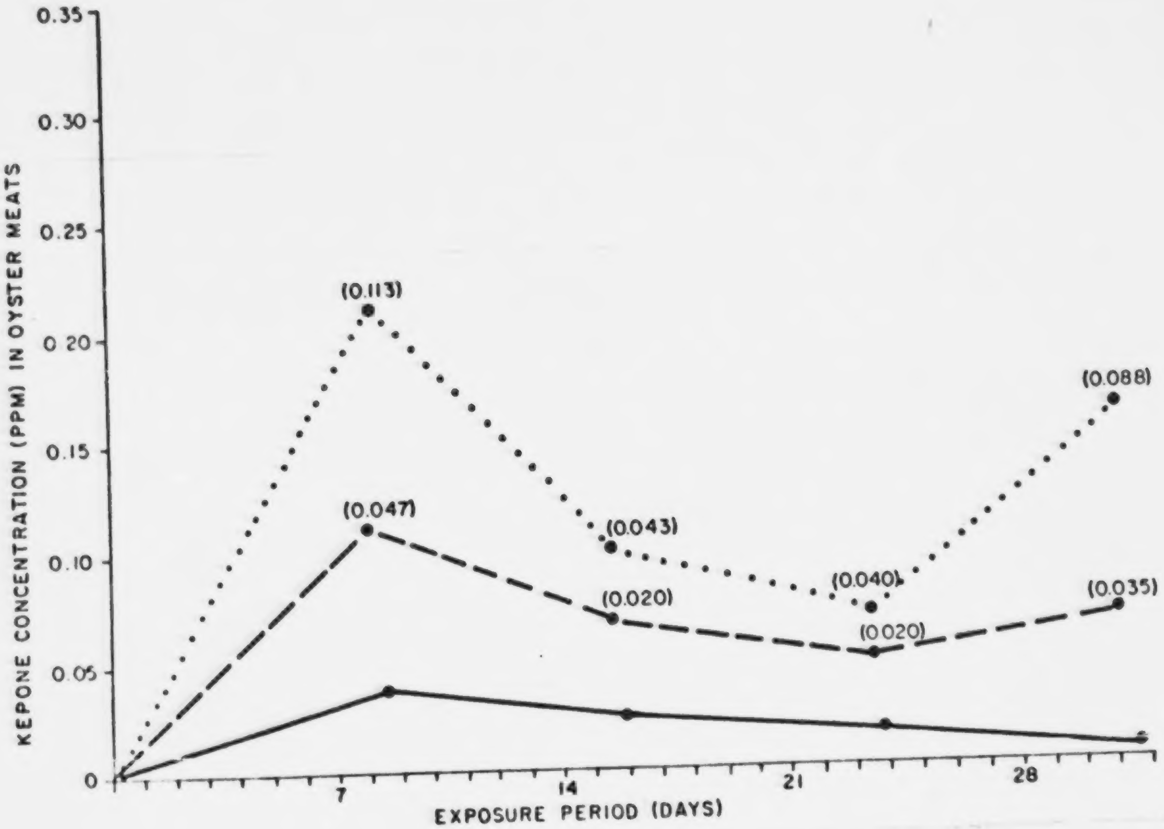


Figure 8. Mean concentration of Kepone in meats of oysters exposed to contaminated sediments in suspension (broken lines) or partially buried in bed of contaminated sediments (solid line). Third series of experiments, 8 July-9 August 1977. Figures in parentheses are mean hourly concentration of Kepone in sediments for weekly period ending at that point.

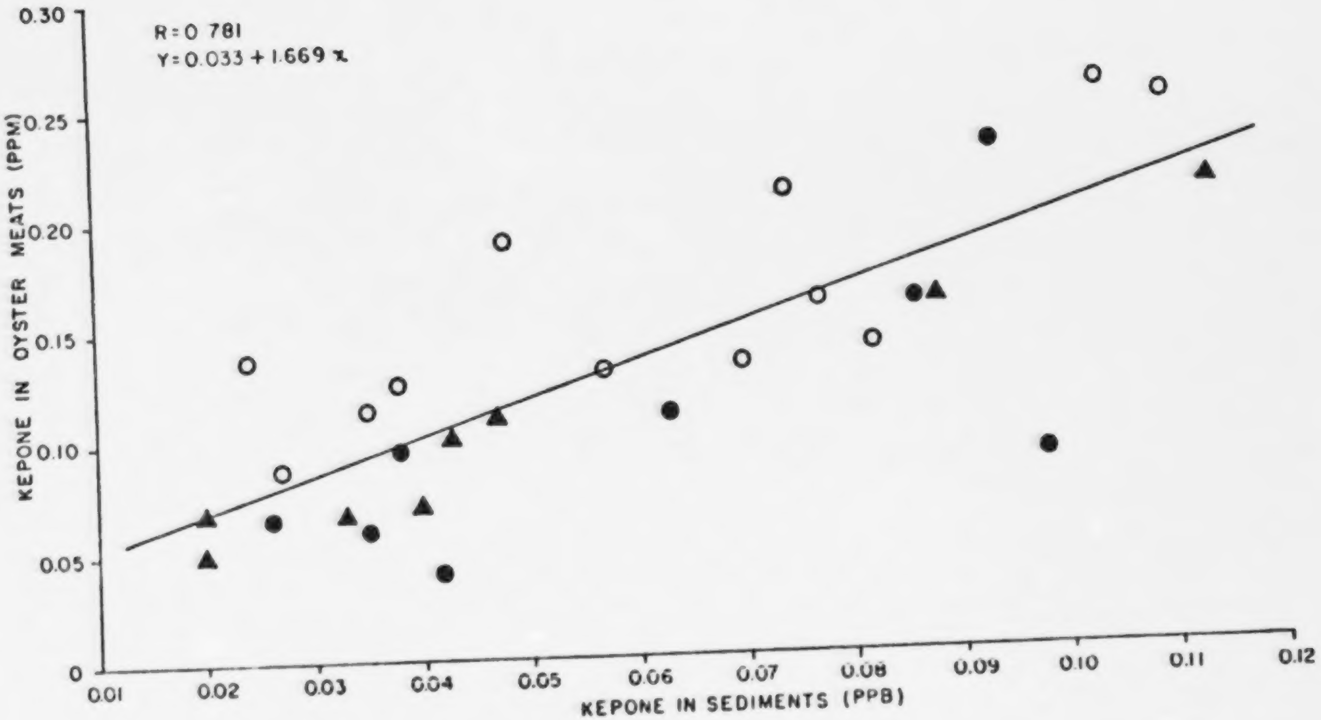


Figure 9. Regression of concentration of Kepone in oyster meats on mean hourly concentration of Kepone in suspended sediments for weekly periods in three series of experiments. Open circles: first series, closed circles: second series, triangles: third series.

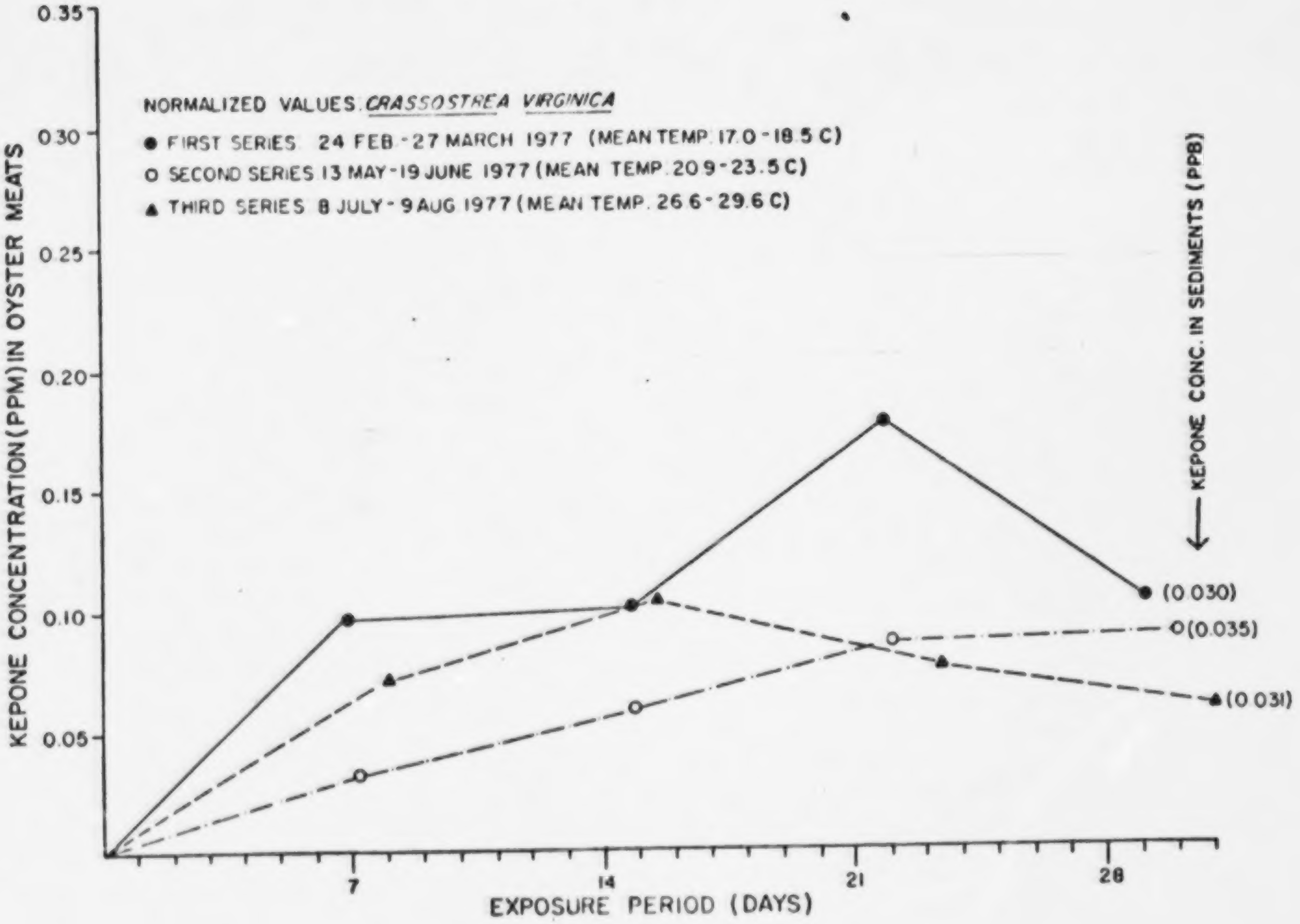


Figure 10. Mean concentration of Kepone in meats of oysters exposed to contaminated sediments in suspension. Normalized a constant hourly concentration for the four-week period in each series. Mean given in parentheses.

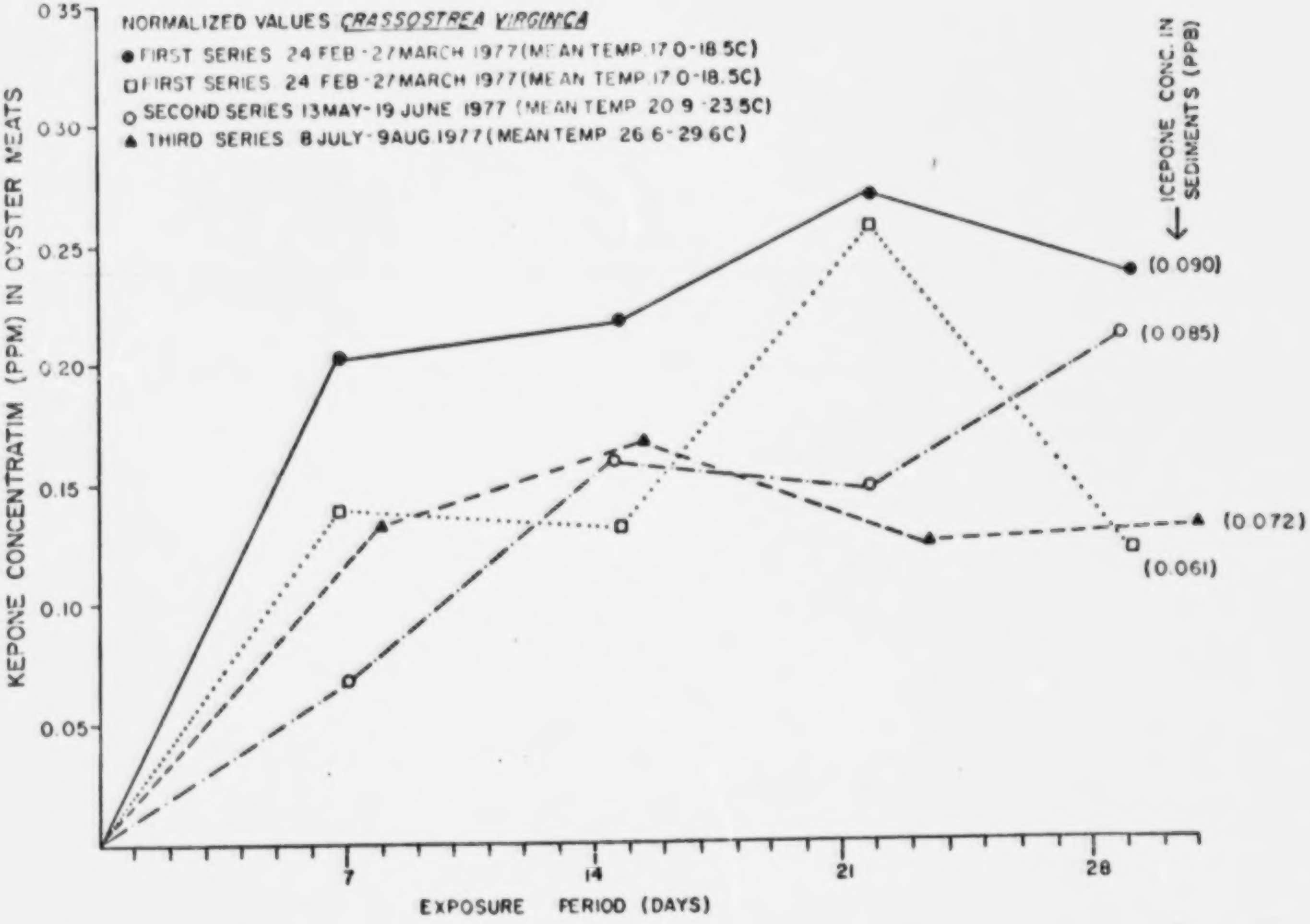


Figure 11. Mean concentration of Kepone in meats of oysters exposed to contaminated sediments in suspension. Normalized to a constant hourly concentration, the mean for the four-week period in each series. Mean given in parentheses.

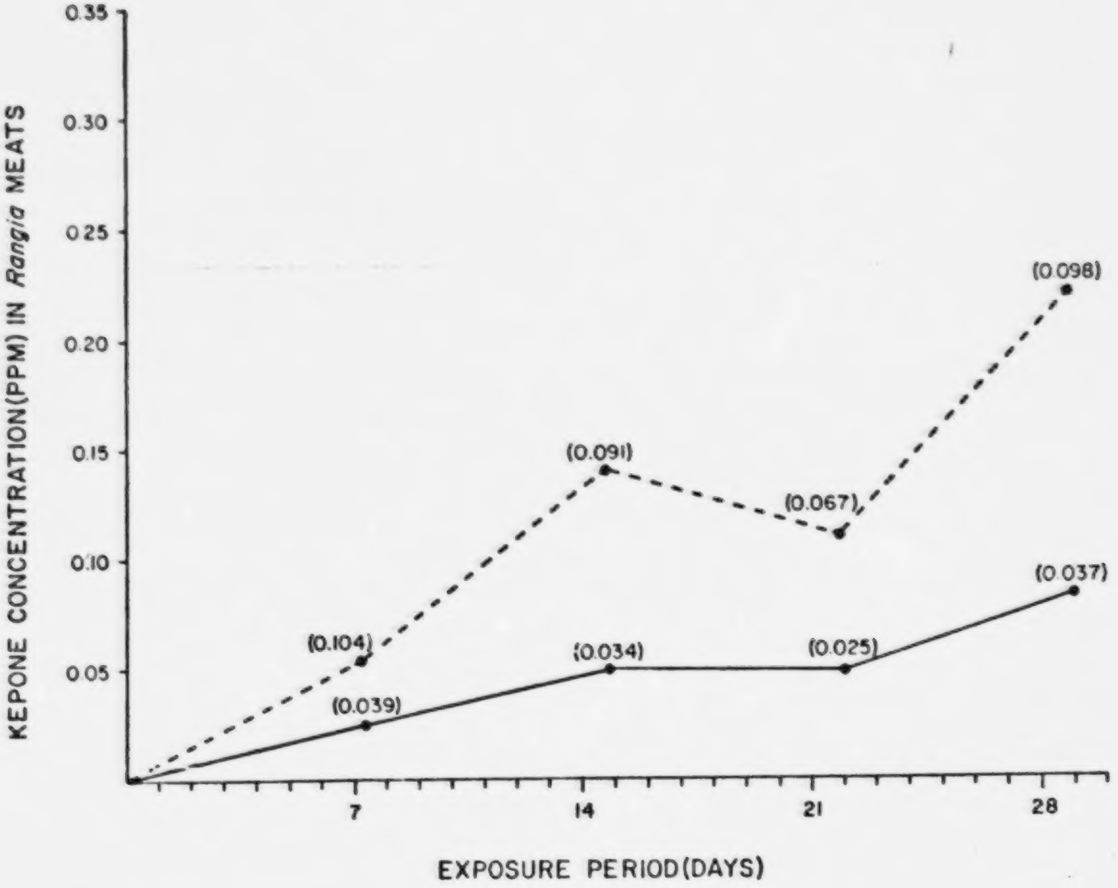


Figure 12. Mean concentration of Kepone in meats of Rangia cuneata exposed to contaminated sediments in suspension. Second series of experiments, 13 May-11 June 1977. Figures in parentheses are mean hourly concentration of Kepone in sediments for weekly period ending at that point.

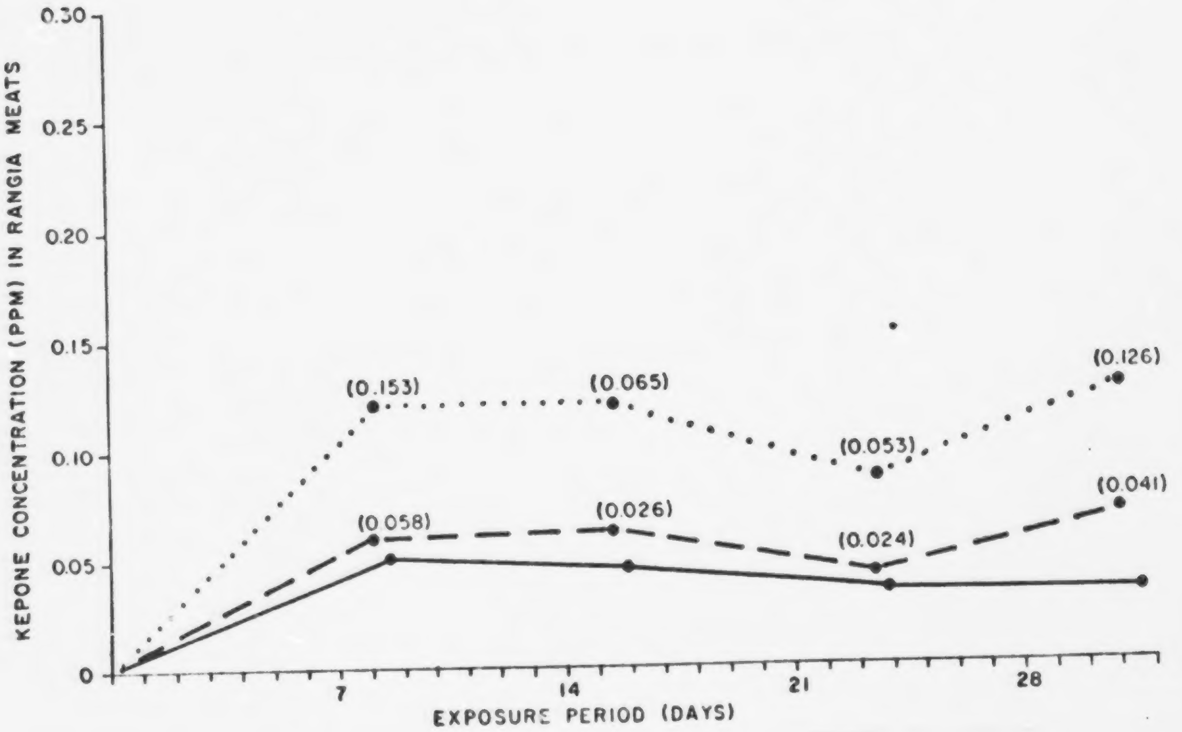


Figure 13. Mean concentration of Kepone in meats of Rangia cuneata exposed to contaminated sediments in suspension (broken lines) or buried in bed of contaminated sediments (solid line). Third series of experiments, 8July-9 August 1977. Figures in parentheses are mean hourly concentration of Kepone in sediments for weekly periods ending at that point.

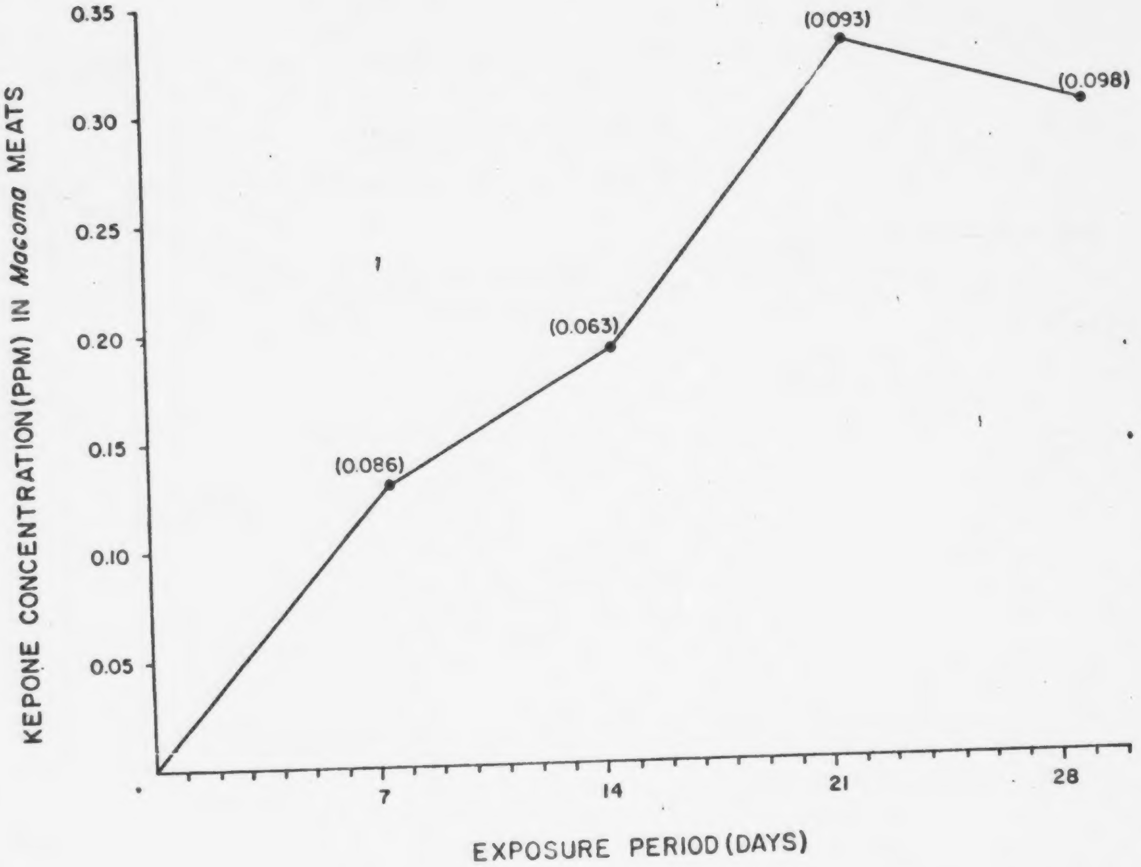


Figure 14. Mean concentration of Kepone in meats of Macoma balthica exposed to contaminated sediments in suspension. Second series of experiments, 20 May-19 June 1977. Figures in parentheses are mean hourly concentration of Kepone in sediments for weekly periods ending at that point.

EPA James River Kepone Hydrographical Survey Study
Progress Report (Nov. 1, 1977)

I. Hydrographical Survey (Aug., 1977)

Four transects were occupied for the field study with three stations included in each transect. The middle (primary) station or primary station, measured top, middle and bottom depth, while the two side channel stations measured top and bottom depths. (figures of the transect positions are included within).

The following is a compilation of information concerning each station.

James River Station, River mile 46.51, sampled from 8/26/77 at 1500 to 8/28/77 at 1800.

Station 46.51A - total depth 17 feet

Current meter depth off the bottom: 2 feet and 7.5 feet

Current meter time in: 8/23/77 at 1015

Current meter time out: 8/29/77 at 1935

Samples taken at mid depth, included all parameters except kepone

Station 46.51 B - total depth 19.5 feet

Current meter depth off the bottom: 3 feet and 10.5 feet

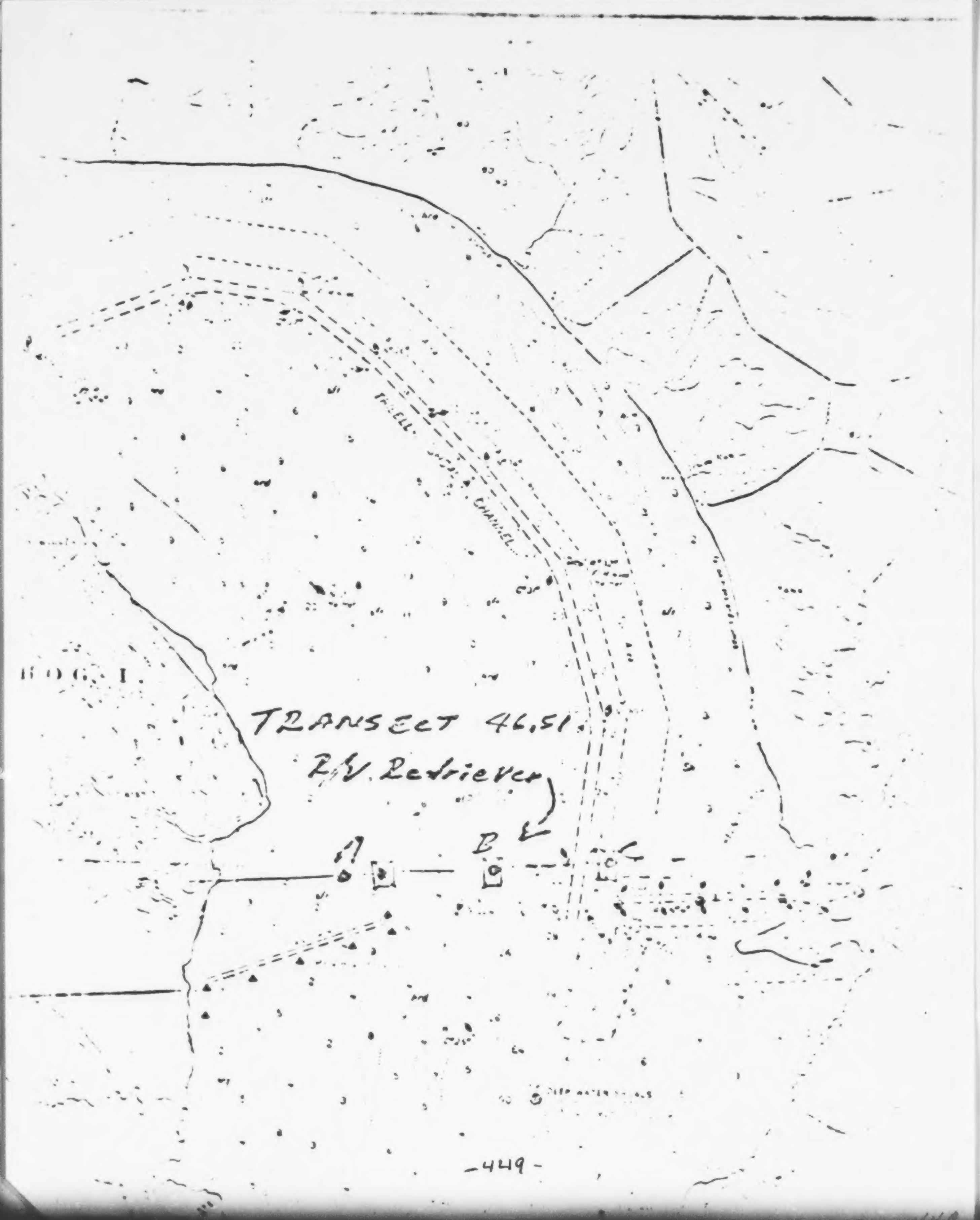
Current meter time in: 8/23/77 at 1050

Current meter time out: 8/29/77 at 1925

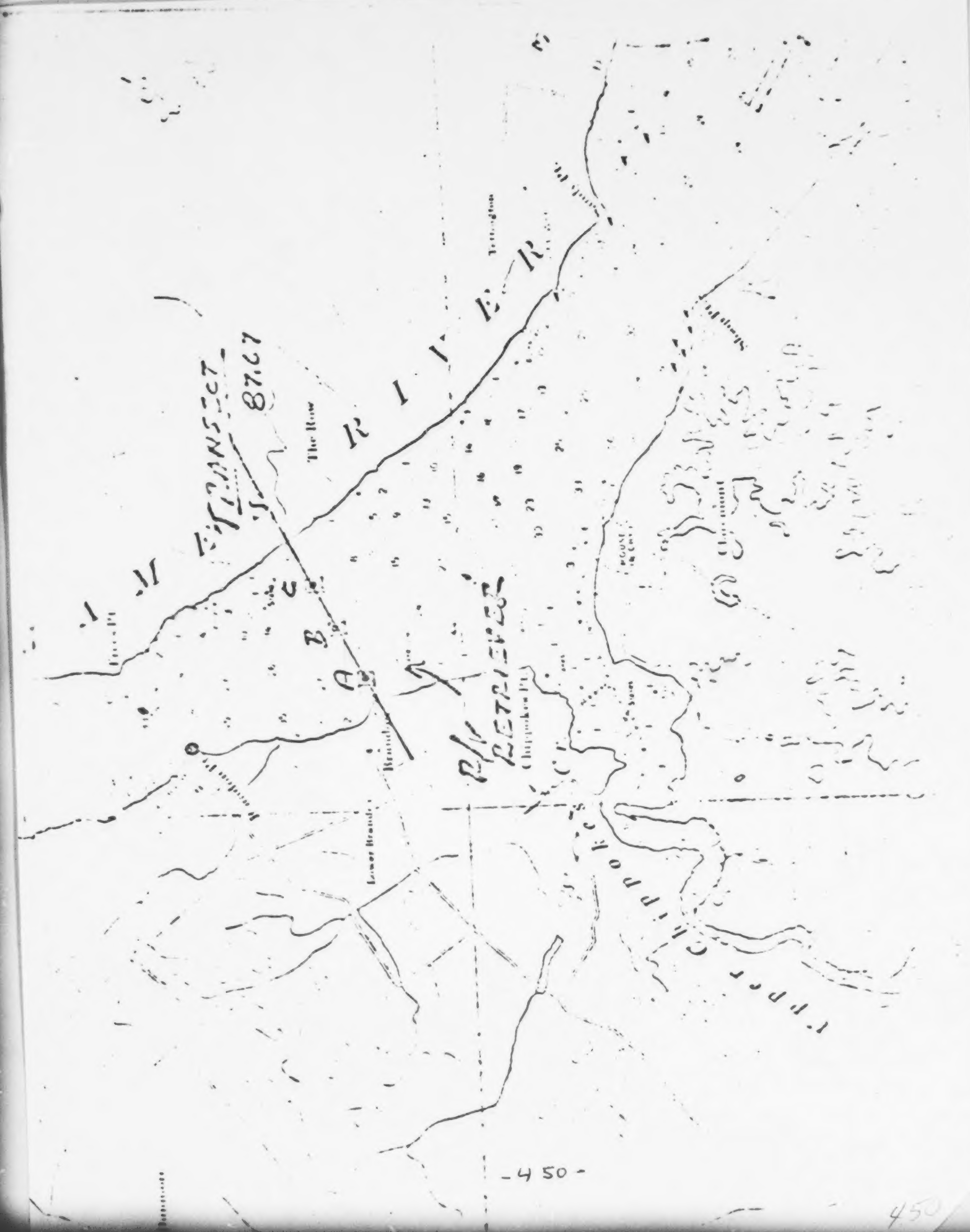
Samples taken at top, mid and bottom depths, included all parameters

Station 46.51 C - total depth 23 feet

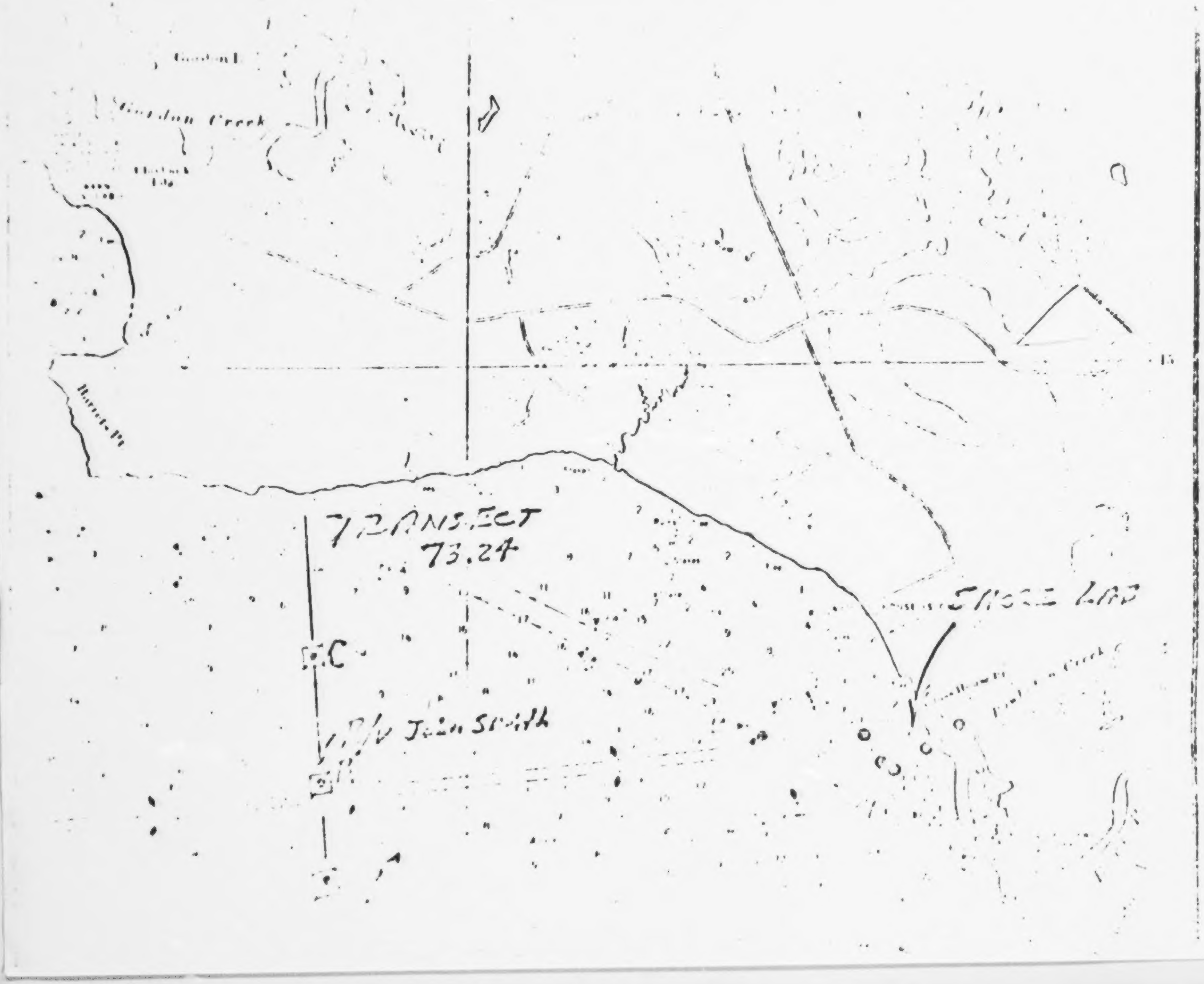
Current meter depth off the bottom: 2 feet, 6.5 feet and 12.5 feet
Current meter time in: 8/23/77 at 0940
Current meter time out: 8/29/77 at 1915
Samples taken at mid depth, included all parameters, except kepone

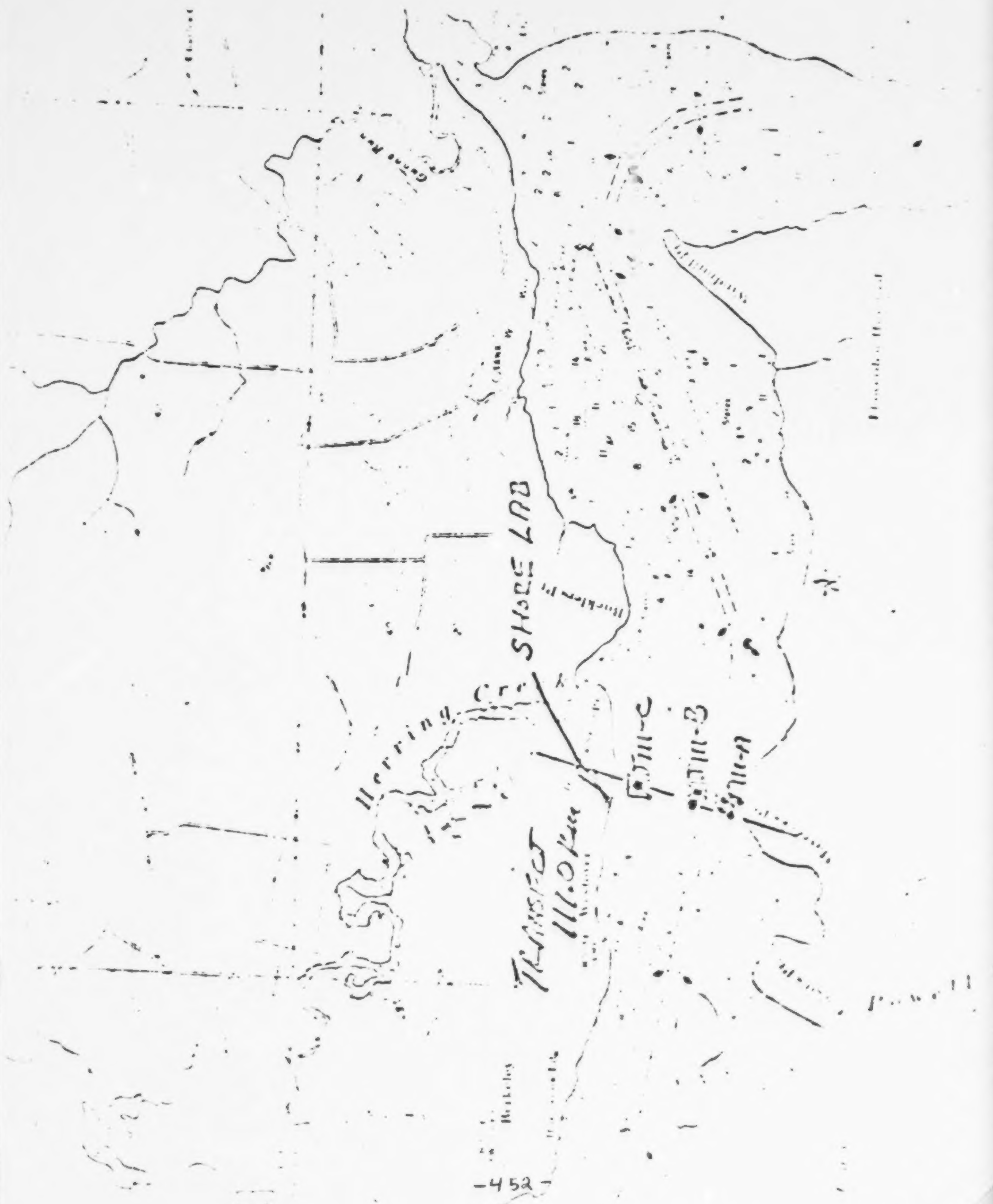

HOG I.
CHANNEL
A
B
C

TRANSECT 46.51.
R/V Retriever

JAMES RIVER
TRANSECT I
87C7
The Row
A
B
C
R/V RETRIEVER
Chippokes Pt
Brandon
Lower Brandon
Upper Chippokes Cr

450


Gordon Creek
TRANSECT
73.24
SHORE LAB
R/V John Smith
C


Herring Creek
SHORE LAB
TRANSECT 111.0 Km
T111-C
T111-B
T111-A
Powell

Station 73.24 sampled from 0800 8/27/77 to 8/29/77 1100

Station 73.24 A - total depth 15.5 feet

Current meter depth off the bottom:
6 feet
Current meter time in:
8/23/77 at 1550
Current meter time out:
8/29/77 at 1523
Samples taken at mid depth, included all parameters except kepone

Station 73.24 B - total depth 21.5 feet

Current meter depth off the bottom:
2.0, 7.5 and 13.0 feet
Current meter time in:
8/23/77 at 1512
Current meter time out:
8/29/77 at 1545
Samples taken from top, mid, bottom, included all parameters

Station 73.24C - total depth 12.5 feet

Current meter depth off the bottom:
5 feet
Current meter time in:
8/23/77 at 1440
Current meter time out:
8/27/77 at 1600
Samples taken at mid depth, included all parameters, except kepone

Station 87.67 sampled from 0900 8/24/77 to 1200 8/26/77

Station 87.67 A - total depth 33 feet

Current meter depth off the bottom:
4, 12.5 and 27 feet
Current meter time in:
8/22/77 at 1620
Current meter time out:
8/29/77 at 1423
Samples taken at mid depth, included all parameters except kepone

Station 87.67 B - total depth 23.5 feet

Current meter depth off the bottom:
4, 9.5, and 16 feet
Current meter time in:
8/22/77 at 1705
Current meter time out:
8/29/77 at 1410
Samples taken at top, mid, bottom, included all parameters

Station 87.67 C - total depth 13.5 feet

Current meter depth off the bottom:
5 feet
Current meter time in:
8/22/77 at 1730
Current meter time out:
8/29/77 at 1404
Samples taken at mid depth, included all parameters, except kepone

Station 111 - sampled from 8/24/77 at 0900 to 8/26/77 at 1200

Station 111 A - total depth 18 feet

Current meter depth off the bottom:
4 and 11 feet
Current meter time in:
8/22/77 at 1350
Current meter time out:
8/29/77 at 1215
Samples taken at mid depth, included all parameters except kepone

Station 111 B - total depth 20 feet

Current meter depth off the bottom:
2, 7.5 and 13 feet
Current meter time in:
8/22/77 at 1140
Current meter time out:
8/29/77 at 1210
Samples taken at top, mid, and bottom depth, included all parameters

Station 111 C - total depth 13 feet

Current meter depth off the bottom:
5 feet
Current meter time in:
8/22/77 at 1215
Current meter time out:
8/29/77 at 1225
Samples taken at mid depth, included all parameters, except kepone

Tide gauges were installed in the following three locations. They were installed one week before the field intensive survey and pulled out one week after the intensive survey. Currently, all tide data are being sent to Fisher and Porter for reduction.

Tide gauge stations:

1) Wooden Pier at Ft. Eustis
2) Pier Chickahominy Holiday Inn Campground
   (off Rt. 5, near mouth of Chickahominy)
3) Westover, Va. Pier (near Hopewell)

II. Data Reduction

All hydrographical and sediment intensive data are currently being keypunched. Parameters include dissolved oxygen, temperature, conductivity, salinity, suspended solids and kepone concentration. It is anticipated to finish keypunching and editing by the end of November, 1977.

Current meter films have been developed and are being prepared to be read. It is also planned to have the data reduction work done by the end of November, 1977.

PRELIMINARY ANALYSIS OF KEPONE DISTRIBUTION IN THE JAMES RIVER

Donald J. O'Connor
Kevin J. Farley

Environmental Engineering and Science Program
Manhattan College
Bronx, New York 10471

Introduction

The general purpose of this research project is to assess the effect of synthetic materials, such as pesticides, on the water quality and ecology of estuarine systems. The present phase of the project is being specifically directed to the analysis of the Kepone distribution in the James River estuary in the vicinity of and downstream from, Hopewell, Virginia. The ultimate goal is to provide a quantitative framework for evaluation of the time required to reduce the Kepone concentrations to acceptable levels.

Significant concentrations of Kepone are present in various phases of the estuarine system of the James River -- in solution, in suspension, in the sediment and in the food chain, particularly in various species of fish. The interrelationships, or more specifically, the transport, uptake and release of Kepone, as shown in Figure II, are thus affected by both physio-chemical mechanisms, as well as bio-ecological phenomena. The former of these includes the hydrodynamic transport through the estuarine system, adsorption to and desorption from the suspended and bed solids, and the settling and resuspension of these solids. The latter incorporates the assimilation and excretion routes through the various components of the food chain. Although less significant for Kepone, transfer to the atmosphere, photochemical oxidation and biological degradation are potentially significant transport and kinetic processes.

JAMES RIVER STUDY AREA

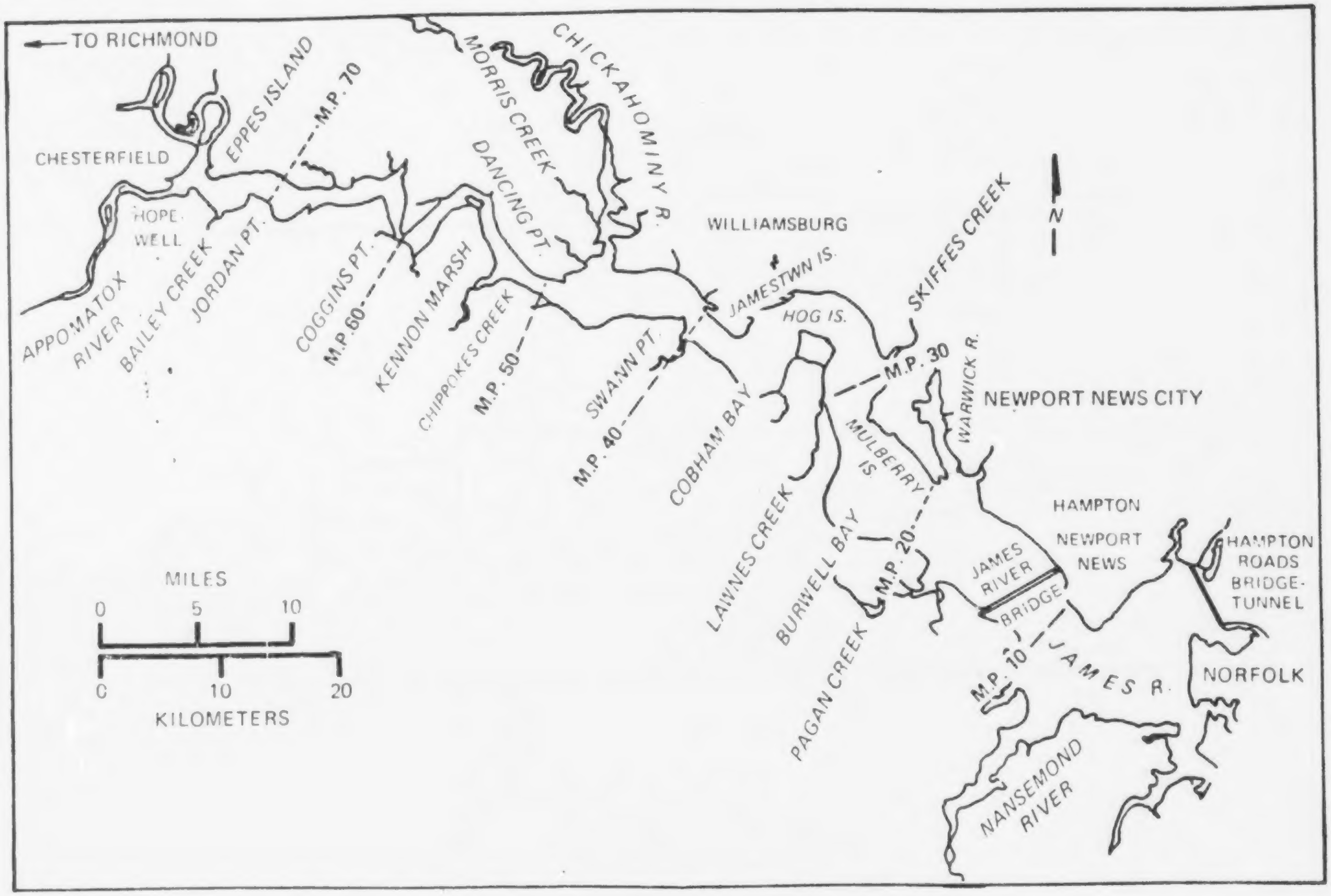

← TO RICHMOND
CHESTERFIELD
EPPES ISLAND
M.P. 70
HOPE WELL
APPOMATOX RIVER
BAILEY CREEK
JORDAN PT.
COGGINS PT.
M.P. 60
KENNON MARSH
CHIPPOKES CREEK
M.P. 50
DANCING PT.
MORRIS CREEK
CHICKAHOMINY R.
SWANN PT.
M.P. 40
WILLIAMSBURG
JAMESTWN IS.
HOG IS.
COBHAM BAY
SKIFFES CREEK
M.P. 30
WARWICK R.
NEWPORT NEWS CITY
N
MULBERRY IS
LAWNES CREEK
BURWELL BAY
M.P. 20
PAGAN CREEK
JAMES RIVER BRIDGE
HAMPTON
NEWPORT NEWS
M.P. 10
JAMES R.
HAMPTON ROADS BRIDGE-TUNNEL
NORFOLK
NANSEMOND RIVER
MILES
0
5
10
0
10
20
KILOMETERS

FIGURE I

JAMES RIVER STUDY AREA

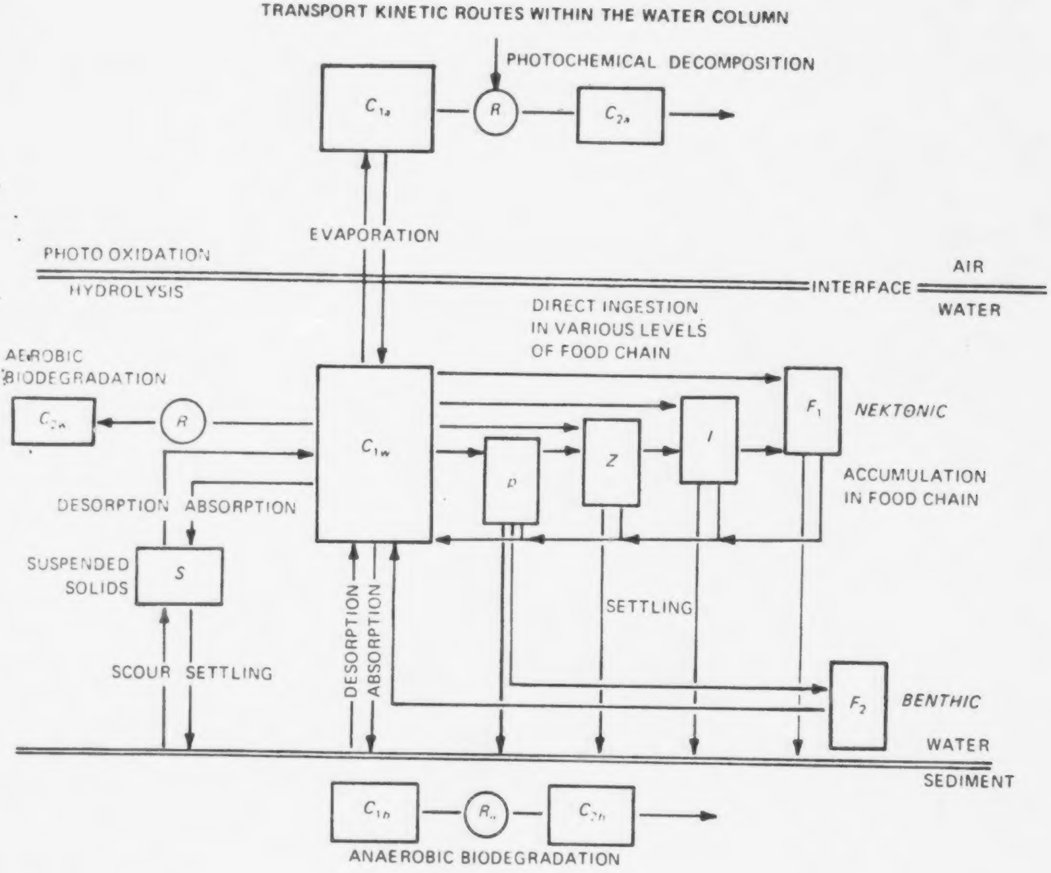

TRANSPORT KINETIC ROUTES WITHIN THE WATER COLUMN
PHOTOCHEMICAL DECOMPOSITION
C_{1a}
R
C_{2a}
EVAPORATION
PHOTO OXIDATION
HYDROLYSIS
INTERFACE
AIR
WATER
DIRECT INGESTION IN VARIOUS LEVELS OF FOOD CHAIN
AEROBIC BIODEGRADATION
C_{2w}
R
C_{1w}
P
Z
I
F_1
NEKTONIC
ACCUMULATION IN FOOD CHAIN
DESORPTION
ABSORPTION
SUSPENDED SOLIDS
S
SCOUR
SETTLING
DESORPTION
ABSORPTION
SETTLING
F_2
BENTHIC
WATER
SEDIMENT
C_{1b}
R_b
C_{2b}
ANAEROBIC BIODEGRADATION

FIGURE II

TRANSPORT - KINETIC ROUTES WITHIN THE WATER COLUMN

The Distribution of Kepone on Solids

Natural clays of various types, and organic material, possess an adsorptive capacity. The rates of adsorptive reactions are being investigated experimentally under controlled laboratory conditions in order to provide realistic kinetic coefficients for the Kepone analysis. The desorptive characteristics of both the inorganic and organic fractions of the suspended solids are also being reviewed. This phenomena of adsorption-desorption is one of the important transfer routes in the ultimate transfer of Kepone from the system. Based on the Langmuir Isotherms, equations have been developed to predict the spatial and temporal distributions of Kepone in an advective-dispersive estuarine system. However, due to the preliminary nature of this work, the less complex, advective, steady state model was used for analysis. Equations governing the water column and estuarine bed for such a system are as follows:

1. Water

Solids $U_1 \frac{\partial m_1}{\partial x} = -K_s m_1 + \alpha K_u m_2$

Dissolved $U_1 \frac{\partial C_1}{\partial x} = -K_o(r_c - r_1)m_1 C_1 + K_d r_1 m_1 - K_b(C_1 - C_2) - K_a C_1$

Particulate $U_1 \frac{\partial P_1}{\partial x} = +K_o(r_c - r_1)m_1 C_1 - K_d r_1 m_1 - K_s r_1 m_1 + \alpha K_u r_2(m_2 - m_1)$

2. Bed

Solids $U_2 \frac{\partial m_2}{\partial x} = +\frac{K_s}{\alpha} m_1 - K_u m_2$

Dissolved $$U_2 \frac{\partial C_2}{\partial x} = -K_o(r_c-r_2)m_2C_2+K_dr_2m_2+K_b(C_1-C_2)$$

Particulate $$U_2 \frac{\partial P_2}{\partial x} = +K_o(r_c-r_2)m_2C_2-K_dr_2m_2+\frac{Ks}{\alpha}r_1m_1-K_ur_2(m_2-m_1)$$

where:

the subscripts 1 and 2 denote the water column and estuarine bed concentrations, respectfully,

and where:

U - horizontal velocity [m/sec]

C - dissolved Kepone concentration [μg/ℓ]

x - longitudinal distance [meters]

K_o - adsorption coefficient [1/(μg/ℓ-day)]

r_c - solids adsorptive capacity [μg/g]

r - Kepone concentration on the solids [μg/g]

m - solids concentration [g/ℓ]

K_d - desorption coefficient [1/day]

K_b - bed diffusion coefficient [1/day]

K_a - aeration coefficient [1/day]

P - solids Kepone concentration [μg/g]

K_s - solids settling coefficient [1/day]

α - the ratio of bed volume to water column volume [dimensionless]

K_u - solids scour coefficient [1/day]

As a first step, this preliminary analysis was simplified by various assumptions - subject to verification by the ongoing field and laboratory studies. The first of these assumptions - solids being in equilibrium i.e. $\frac{\partial m_1}{\partial x}$ and $\frac{\partial m_2}{\partial x} = 0$, appears to be a safe assumption for the non-saline portion of the estuary. In addition, the bed solids concentration, m_2, was said to be much greater than the suspended solids concentration, m_1; the aeration term, K_a, was taken to be negligible; and the solids adsorptive capacity, r_c, was assumed to be much greater than either of the Kepone concentrations on the solids, r_1 and r_2. The kinetic coefficients - K_o, K_d, K_s, and K_u, were assigned from the limited data available. Finally, for this "first-cut" model, the Kepone concentrations on the bed solids, r_2, were assigned from data; these concentrations were in turn utilized in predicting the Kepone water column concentrations.

Based on these assignments of coefficients, the longitudinal distribution of total and dissolved Kepone in the water column is presented in Figure III along with the State Water Control Board 1976 Kepone data. The line of total Kepone concentration fits the data quite well and although the dissolved fraction of Kepone is high, this concentration is merely a function of Kepone kinetic coefficients, K_o and K_d - values which were obtained from a minimal amount of sketchy data. Further analysis is presently being performed which will predict both the water column and the bed concentrations of Kepone.

The above analysis will be further complicated as the

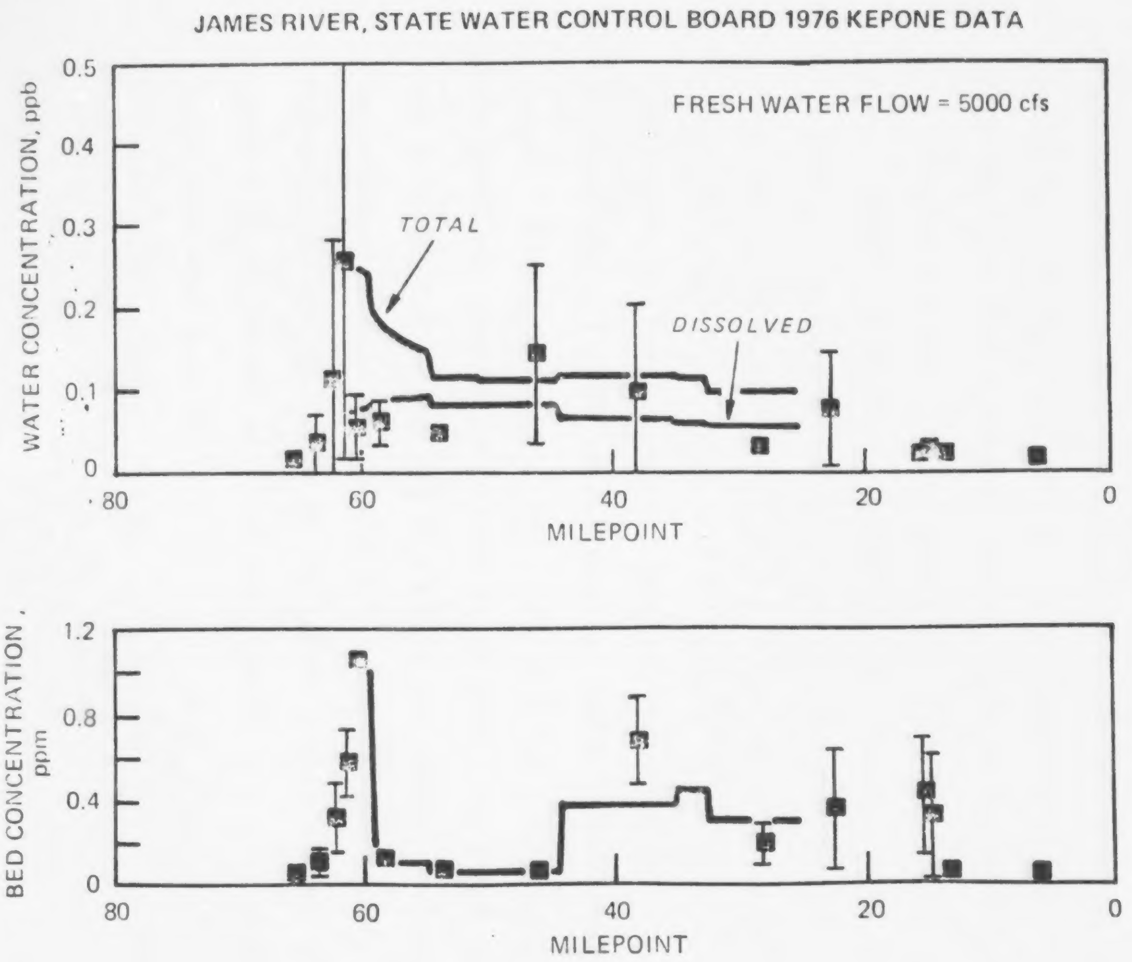


FIGURE III

KEPONE CALCULATION FOR THE JAMES RIVER ESTUARY (1976) saline portion of the estuary is approached. As the lighter clay particles which are maintained in suspension in the non-saline area encounter the saline region of the estuary, flocculation and agglomeration may occur, increasing the size and possibly the density of the particles. These factors result in further deposition, which is enhanced by virtue of their occurrence in the null zone of the estuary. There are, therefore, a variety of significant factors which may account for the accumulation of solids and Kepone in the estuarine bed at the fresh water-saline interface. These factors, along with the inability to assume solids equilibrium in the saline region, have lead to a detailed investigation of solid material in the estuary.

Hydrodynamic Transport

Since the concentration of suspended solids is an important factor as an accumulation site for Kepone, the temporal and spatial distribution of the solids within the estuarine system is a necessary element in the analysis. The distribution is determined by the hydraulic transport through the estuarine system. A two-dimensional (longitudinal-vertical) analysis has been developed, based on the fundamental principles of momentum, continuity and state.

In this analysis, under steady state, tidally averaged conditions, the longitudinal momentum equation for a laterally homogeneous estuary is:

$$0 = \frac{1}{\rho}\frac{\partial p}{\partial x} + N\frac{\partial^2 u}{\partial z^2} \qquad (1)$$

where ρ = density; p = pressure; N = vertical eddy viscosity; and u = horizontal velocity. The coordinates for Eq. 1 are shown in Fig. IV in which the longitudinal x-axis is positive toward the ocean and the vertical z-axis is positive toward the bed of the estuary channel. Boundary conditions compatible with Eq. 1 are,

$$\frac{\partial u}{\partial z} = 0 \qquad \text{at } z = -n \qquad (2)$$

$$-N\frac{\partial u}{\partial z} = C_d/u_b/u_b \qquad \text{at } z = h \qquad (3)$$

in which $-n$ = surface elevation and h = average depth; C_d = dimensionless friction coefficient; and u_b = velocity at the bed. The vertical component of the momentum equation is simply the hydrostatic pressure equation:

$$\frac{1}{\rho}\frac{\partial p}{\partial z} = g \qquad (4)$$

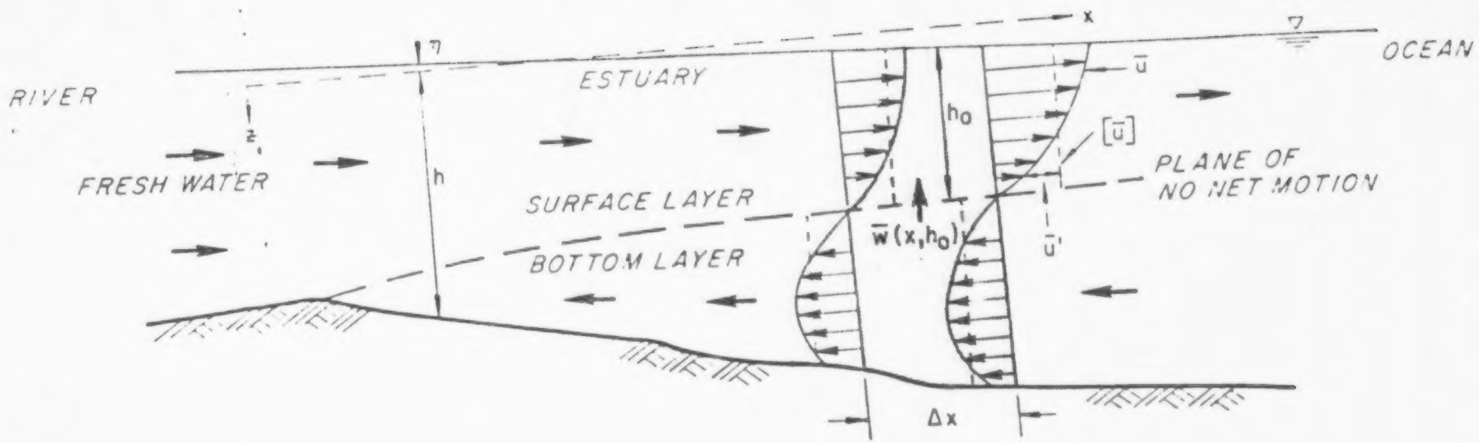

RIVER
FRESH WATER
η
z
h
ESTUARY
SURFACE LAYER
BOTTOM LAYER
x
h_0
$\bar{w}(x,h_0)$
$\bar{u}$
$[\bar{u}]$
$\bar{u}'$
PLANE OF
NO NET MOTION
OCEAN
Δx

FIGURE $\overline{IV}$

SCHEMATIC DIAGRAM OF TWO-DIMENSIONAL ESTUARINE CIRCULATION

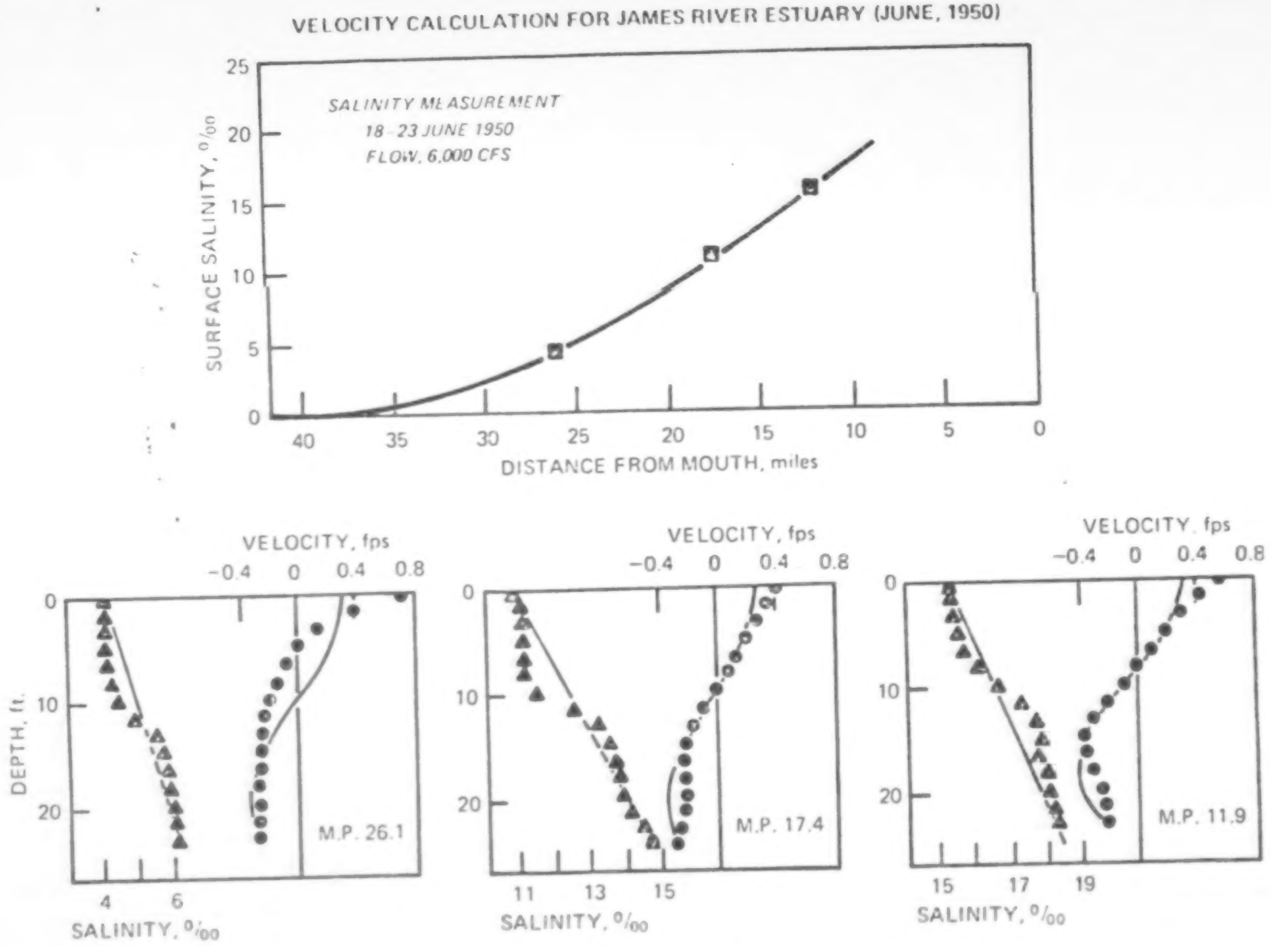
In order to solve Eq. 1, the hydrostatic pressure, Eq. 4, is expressed in terms of the horizontal and vertical distribution of salinity. The equation of state which specifies the density as a function of salinity is given by:

$$\rho = \rho_f(1 + \alpha\bar{C}) \qquad (5)$$

in which ρ_f = the density at zero salt content and $\alpha = 0.000757$ (parts per thousand)$^{-1}$. The components of the pressure force are then evaluated in terms of the observed vertical and longitudinal salinity gradients and freshwater flow, which are assumed known from measurement.

The solution of the above equations indicates that local rather than boundary conditions control the magnitude and gradient of horizontal velocity at a particular location. Because of local control, the velocity at one location is relatively independent of those at other locations. This condition occurs as a result of decoupling the equations of motion and salt transport.

Results of this analysis are presented for Pritchard's June 1950 survey and Nichols' March 1965 survey of the James River in Figure V and VII respectfully. In addition, the solution also indicates the depth at which the net horizontal velocity is zero. Defining this depth at a number of stations and interpolating for others delineates the plane of no net motion for the saline intrusion zone of the estuary, Figures VI and VIII. At the tail of the salinity intrusion, this plane meets the bed of



NOTE: SALINITY AND VELOCITY MEASUREMENTS BY THE CHESAPEAKE BAY INSTITUTE

FIGURE $\overline{\text{V}}$

VELOCITY CALCULATION FOR JAMES RIVER ESTUARY (JUNE, 1950)

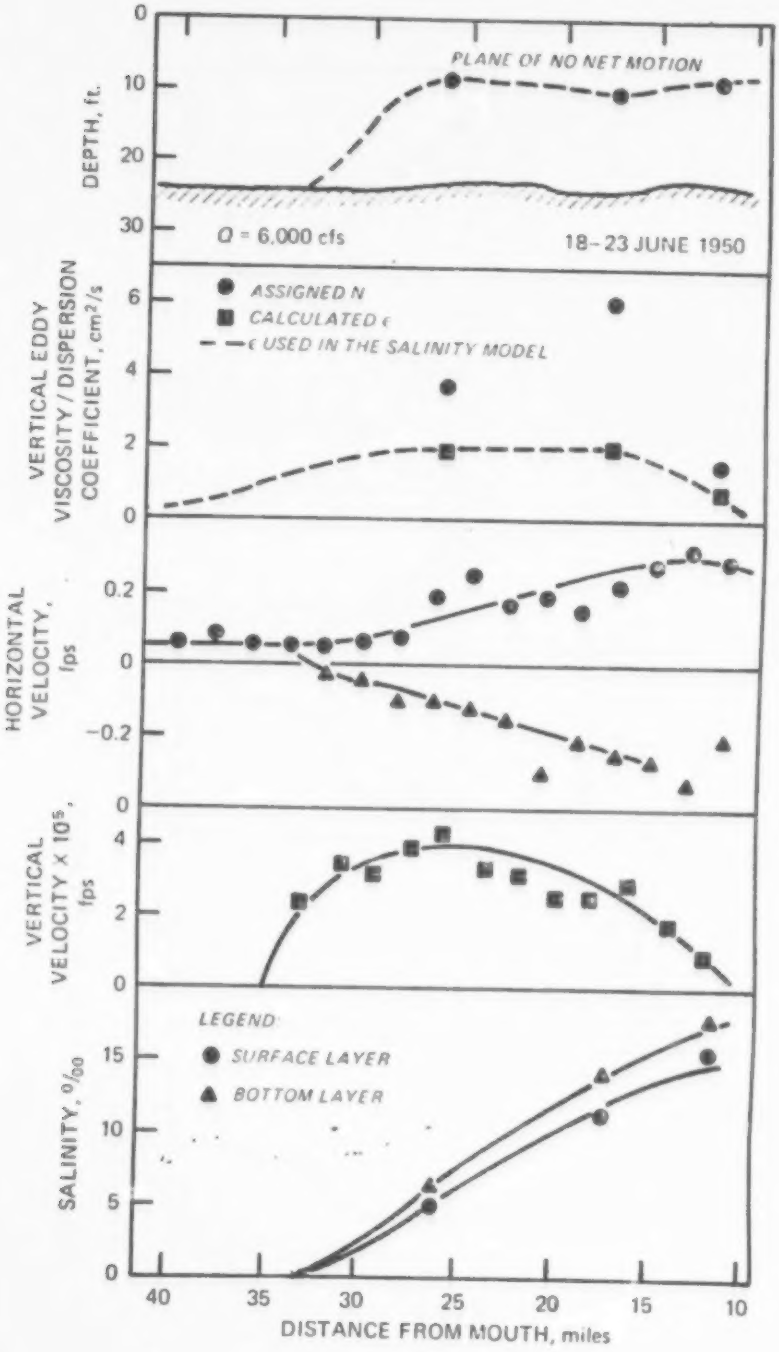
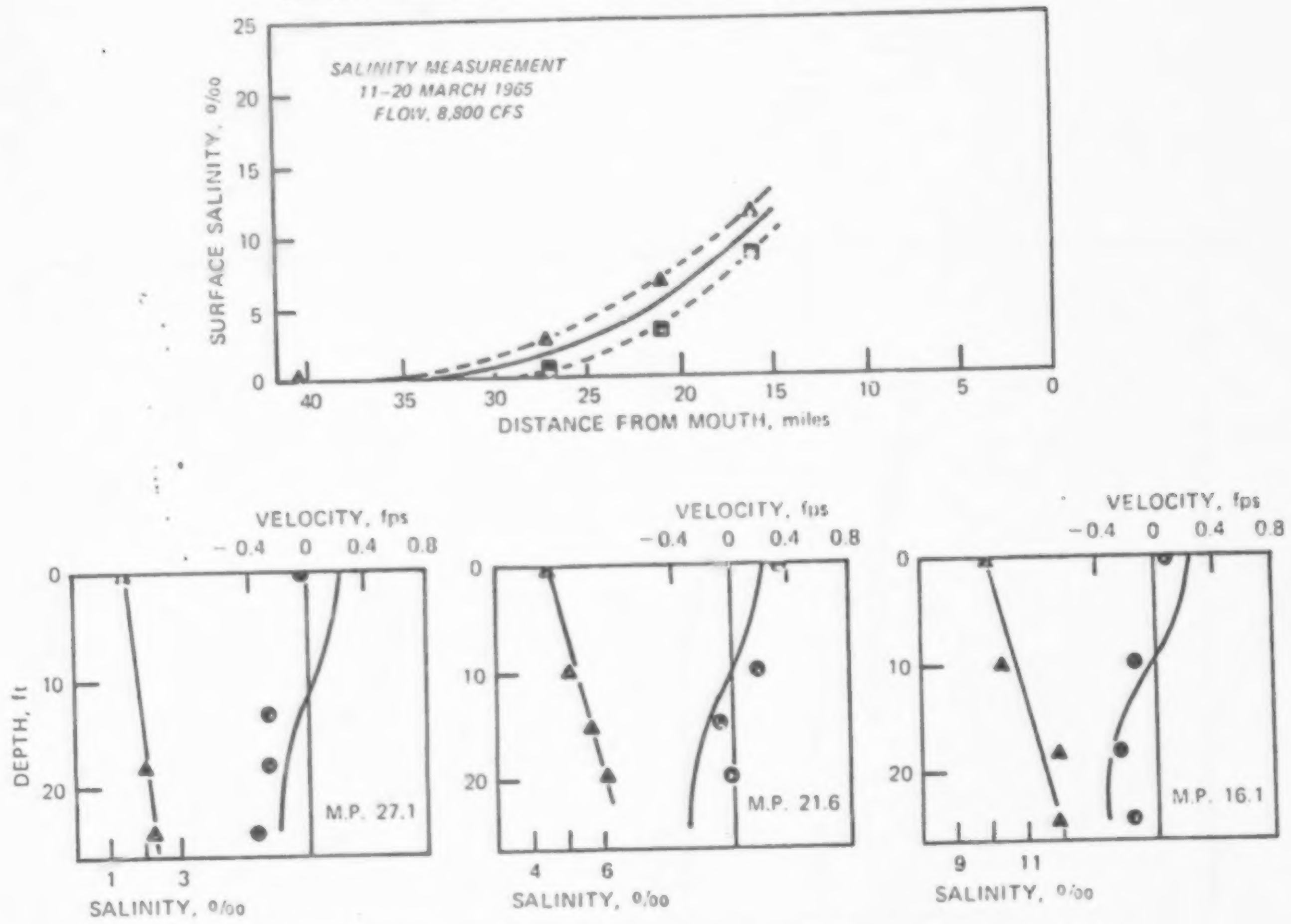

SALINITY CALCULATION FOR JAMES RIVER ESTUARY (JUNE, 1950)

FIGURE $\overline{\text{VI}}$

SALINITY CALCULATION FOR JAMES RIVER ESTUARY (JUNE, 1950)


VELOCITY CALCULATION FOR JAMES RIVER ESTUARY (MARCH, 1965)

NOTE: SALINITY AND VELOCITY MEASUREMENTS BY THE VIRGINIA INSTITUTE OF MARINE SCIENCE

FIGURE VII

VELOCITY CALCULATION FOR JAMES RIVER ESTUARY (MARCH, 1965)

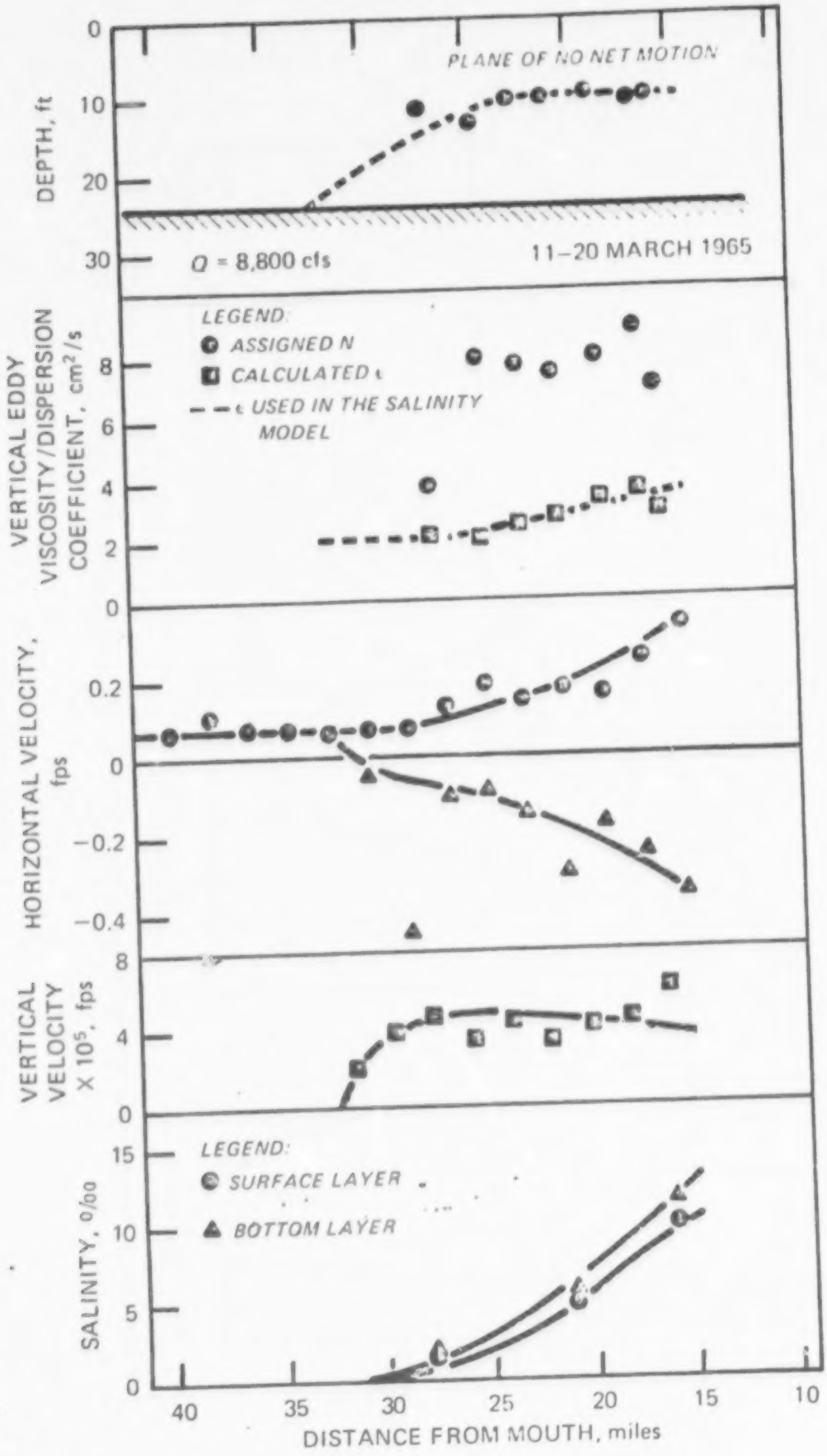


FIGURE VIII

SALINITY CALCULATION FOR JAMES RIVER ESTUARY (MARCH, 1965) the estuary. Upstream of this area, the horizontal velocity in the whole water column is in the seaward direction.

The estuary is then segmented horizontally and the horizontal flow in the surface layer at each vertical cross section is first calculated. Horizontal flow difference between two adjacent vertical planes gives the vertical flow between the surface and bottom layer, from which the vertical velocity is obtained by dividing by the average width of the segment. This procedure is obviously a solution of the hydraulic continuity.

The vertical flux of salt due to dispersion between the surface and bottom layers is described by the dispersion coefficient, ε, obtained from the vertical eddy viscosity through an empirical relationship,

$$\varepsilon = N(1 + R_i)^{-1} \tag{6}$$

where Ri (Richardson number) is defined as:

$$Ri = \frac{g\frac{\partial\rho}{\partial z}}{\rho(\frac{\partial\bar{u}}{\partial z})^2} \tag{7}$$

Equation 6 indicates the relationship between the two coefficients, whose general validity has been shown by field data, as presented by Officer.

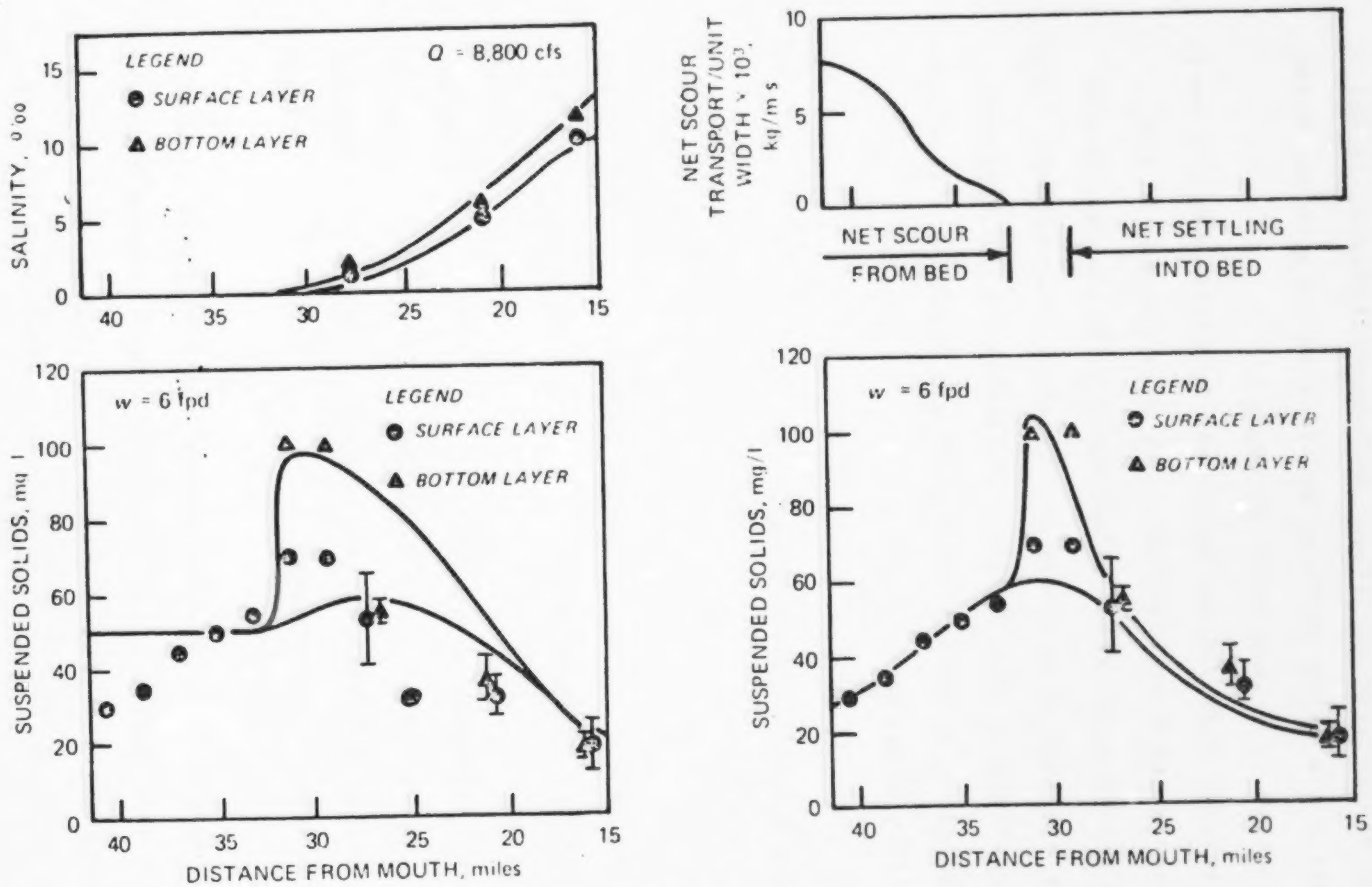
The tidal diffusion and velocity shear contributions, which can be envisioned collectively as a longitudinal dispersion across a vertical section following the classical one-dimensional estuarine analysis, did not exhibit themselves in the portion of the estuary that our models were concerned.

The distribution of salinity was used to test the validity of the hydrodynamic model - bottom panels of Figures VI and VIII. Based on these validations of the hydrodynamic model, an analysis of suspended solids followed by incorporating the settling and scour rates with the hydrodynamic transport to determine the distribution of solids. Settling rates, for the present, were assumed constant down the length of the estuary and this rate was obtained from the average particle size, using a modification of Stokes' Law. Since little work has yet been performed on scouring rates in estuaries, these rates were assigned merely to show that a good fit can be obtained. Results of this solids modeling, with and without the assigned scouring rates, are presented in Figure IX.

ASSIMILATION AND DEPURATION OF KEPONE IN THE FOOD CHAIN

The transfer of Kepone from its initial discharge at Hopewell to its accumulation in the fishery stock may occur in a number of ways. It may be ingested directly from that which is dissolved or suspended in the water; it may be assimilated by the phytoplankton-zooplankton; and it may be taken in by bottom feeders from the material which has settled in the channel bed. The predominant sites for settling appear to be downstream from Hopewell, in the region of the fresh water-saline interface, and in various dead zones in the fresh and saline regions. Experiments involving assimilation and depuration of Kepone by various species are being conducted. The rates of accumulation and

SUSPENDED SOLIDS CALCULATION FOR JAMES RIVER ESTUARY (MARCH, 1965)



NOTE SUSPENDED SOLIDS MEASUREMENTS BY THE VIRGINIA INSTITUTE OF MARINE SCIENCE

FIGURE IX

SUSPENDED SOLIDS CALCULATION FOR JAMES RIVER ESTUARY (MARCH, 1965) excretion, equilibrium conditions and concentrations, lethal and chronic - are being analyzed in order to incorporate these kinetic factors in a food chain analysis.

Preliminary analysis has been made in evaluating the assimilation and depuration kinetics on various species of fish. Data from experimental studies performed at EPA's Gulf Breeze Laboratory are used to evaluate the relevant coefficients. The equation utilized in this analysis - similar to the Langmuir kinetic equation for the adsorption to and desorption from suspended solids, is as follows:

$$\frac{\partial (rm)}{\partial t} = K_o(r_c - r)m(t)C - K_d rm(t)$$

where

r - Kepone concentration in the biomass [µg/g]

m - biomass concentration [g/ℓ]

t - time [days]

K_o - assimilation coefficient [1/day]

r_c - biomass assimilation capacity [µg/g]

C - dissolved Kepone concentration [µg/ℓ]

K_d - depuration coefficient [1/day]

The only assumption made in this analysis was that the biomass assimilation capacity, r_c, was taken to be much greater than the Kepone concentration in the biomass, r. Results of this analysis for oysters (Crassostrea, virginica) are presented in Figure X.

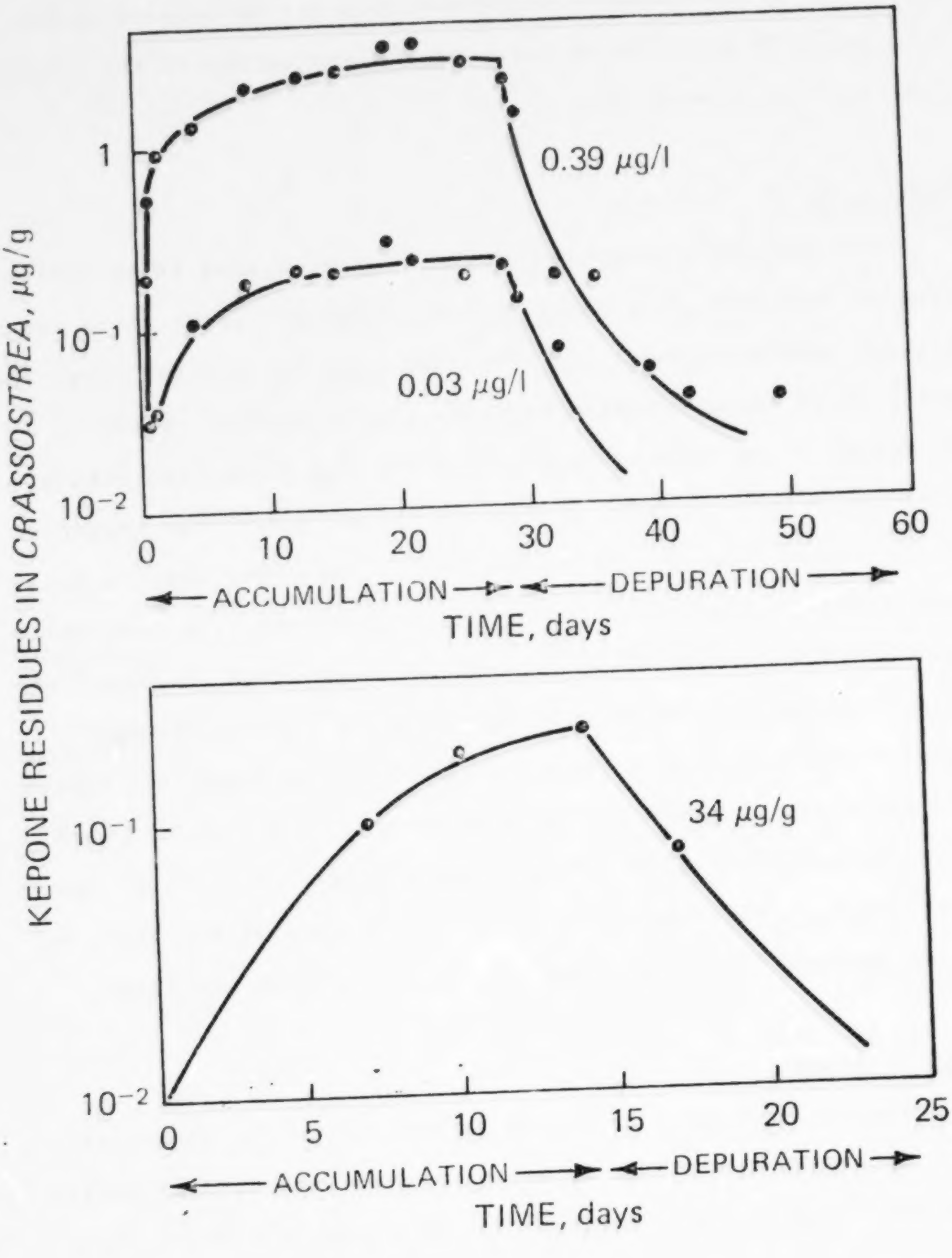


FIGURE X

CALCULATION FOR THE ASSIMILATION AND DEPURATION OF KEPONE IN OYSTERS

From these results, it can be shown that the bio-ecological phenomena of assimilation and depuration can be modeled utilizing Langmuir kinetics if data for the evaluation of the relevant coefficients is available.

CONCLUSION

The equations presented in this report appear to be sufficiently realistic as a first approximation in representing the various phenomena under consideration. At the present time, the analysis is being extended to treat the ecological system as a continuum using trophic length as a metric. Given the inputs from the sources in the vicinity of Bailey's Bay, the transport in the non-saline and saline regions of the James estuary and the distribution of suspended solids and Kepone, the food chain model is being enlarged to include the uptake and excretion of Kepone in the various trophic levels and the predation and feeding associated with these levels. At this time, the saline and non-saline regions of the estuary are being combined into one continuous solution. Steady state conditions, which represent average conditions during various seasons of the year, are being assumed for these preliminary steps of the analysis.

ACKNOWLEDGEMENTS

The research work described in this report is sponsored by Gulf Breeze Research Laboratory, Sabine Island, Gulf Breeze Florida, Grant Number R804563. The participation of Gerald L.

Schnoor is acknowledged. Various phases of the computations were performed by Cherng-Ju Kim and George A. Leahy, research assistants in the Environmental Engineering and Science Program at Manhattan College.

SESSION V

"Additional Presentations and Wrap-up"

CHAIRMAN

J. Gary Gardner
Regional Toxic Substances Coordinator
U.S. Environmental Protection Agency, Region III

SPEAKERS

Mr. Charles H. Whitlock
NASA Langley Research Center
"Remote Sensing Observations of Industrial Plumes at Hopewell, Virginia"

Dr. A. R. Paterson
Research Manager
Allied Chemical Corporation
"Allied Chemical Kepone Investigations"

Mr. Martin W. Brossman
Wrap-up, EPA Activities with Kepone

REMOTE SENSING OBSERVATIONS
OF INDUSTRIAL PLUMES
AT HOPEWELL, VIRGINIA

by

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INTRODUCTION

The National Aeronautics and Space Administration (NASA) is investigating the potential of remote sensing for monitoring various parameters in the marine environment in cooperation with the Environmental Protection Agency (EPA) under Interagency Agreement IAG-0245. One aspect of this effort is a research program aimed at developing remote sensing strategies for the monitoring of industrial outfalls. Recent EPA field studies have shown that 98 percent of all water discharge points are detectable by changes in color or temperature which may be monitored using remote sensing instrumentation.[1]

Over the past several years, a series of aircraft remote sensing experiments have been made over the James River at Hopewell, Virginia. The objective of these flights has been to investigate the potential of various types of remote sensing instruments for identification and quantification of several water parameters. Aerial mapping cameras were carried on each of the aircraft experiments, and a thermal band was part of the multispectral scanner data for all flights except one. It is the purpose of this document to synthesize the photographic and thermal data which are presently available, such that appropriate agencies may assess their value to solution of the Kepone problem in a timely manner. Industrial outfall plume patterns over a wide range of tidal and river flow conditions are presented. A description of the aerial photography system which gave the best images is also provided.

EXPERIMENTAL CONDITIONS

The Langley Research Center has conducted a total of 30 aircraft remote sensing overpasses in the Hopewell area with mapping-quality camers and multispectral scanner instruments. Table 1 summarizes the environmental conditions and type of data obtained for each experiment.

TABLE 1.
SUMMARY OF
HOPEWELL, VA. REMOTE SENSING DATA

DATE	Feb. 1, 1974	May 28, 1974	May 17, 1977
WIND SPEED	5 kts	10 kts	<3 kts
WIND DIRECTION	E-NE	NW	SW(am) NE(pm)
JAMES RIVER DISCHARGE (AVERAGE = 7,432 cfs)	14,028 cfs	5,306 cfs	2,808 cfs
APPOMATTOX RIVER DISCHARGE (AVERAGE = 1,590 cfs)	1,780 cfs	786 cfs	580 cfs
NUMBER OF OVERPASSES			
PHOTO	1	5	24
SCANNER WITH THERMAL	0	1	24
TIDE AT OVERPASS (CITY POINT)	MAX EBB (3.7 HRS AFTER HIGH)	0.9-2.0 HRS AFTER HIGH	INCOMING TIDE (1.7 HRS BEFORE LOW TO 1.5 HRS AFTER HIGH)

The first experiment was conducted February 1, 1974, and consisted of a single overpass. A mapping camera was used along with an experimental multispectral scanner; however, that particular scanner did not have a band for thermal measurements. Wind was out of the east-northeast and river discharge was higher than average.[2] Flight overpass occurred with an outgoing tide near the time of maximum ebb.

The second experiment occurred on May 28, 1974. The mission included five overpasses with mapping quality photography and one overpass with a multispectral scanner having a band for thermal measurements.[3] Wind was out of the northwest and river discharge was below average.[2] Again the overpasses occurred on an outgoing tide.

The third experiment occurred on May 17, 1977, and included 24 overpasses over a 9-hour period. This experiment was a cooperative effort between NASA, the Virginia State Water Control Board, and the U.S. Army Corps of Engineers. Winds were very low and shifted in direction. River discharge measurements furnished by the Virginia State Water Control Board indicate low river flow conditions. Overpasses began 1.7 hours before low tide, covered the incoming flow, and ended 1.5 hours after high water.

A detailed description of tidal conditions at time of remote sensor overpass is shown in figure 1. For ease of presentation, overpass times are given in hours after high tide at City Point. From figure 1, it is clear that remote sensing data have been obtained over most of the tidal cycle. It must be re-emphasized, however, that river flow and wind conditions were different on each of the days that experiments were conducted so caution is required in making a direct comparison of flow patterns. In the discussion which follows, flow patterns are presented in the order shown in figure 1. For reasons of brevity, data from all overpasses are not shown. For the May 28, 1974, data, photographic results are presented for the overpass at 0.9 and 1.7 hours. Thermal images are shown for the overpass at 2.0 hours. Photographic results are shown for the February 1, 1974, overpass as well as for the overpasses at 6.9, 8.4, 11.9, and 1.5 hours after high tide from the May 17, 1977, experiment. As indicated in table 1, thermal measurements were made for the May 17, 1977, experiment but are not available at the present time.

RESULTS

A photograph of the May 28, 1974, overpass at 0.9 hour after high tide is shown in figure 2. The original imagery was taken on Kodak natural color aerial film from an altitude of 5.3 kilometers. Unfortunately, the photographic and report reproduction process results in a considerable loss of contrast, such that only gross features of the plume are evident. Second-generation transparencies (copied from the original negative) do show a marked contrast between the Gravelly Run and Bailey Creek plumes however. Distinction is possible because of the different colors of the two discharges.[4]

To enable a reproducible presentation of the Gravelly Run and Bailey Creek plumes, the second-generation transparencies for February 1, 1974, May 28, 1974, and May 17, 1977, were copied on tracing paper for the region from the mouth of the Appomattox River to beyond Tar Bay. These sketches are meant to convey the general limits of the plumes but are not intended to relate to specific pollutant concentrations or those subtle tonal variations that are visible only on the originals. Figure 3 shows the completed sketch for the overpass at high tide plus 0.9 hour on May 28, 1974. The gray shading generally denotes the black water masses of the same color as being discharged from Bailey Creek. The Gravelly Run plume is denoted by the dotted areas. Sketches of plume patterns were made only for those situations where water depths were believed greater than remote sensing penetration depths. Secchi depth observations (an indicator of the penetration depth) of Bailey Creek at low tide from the Route 10 bridge were on the order of 8 cm (3.1 in). Thus, the bottom was not visible in the aerial photographs for all but the immediate shoreline areas. The sketches, therefore, represent plume patterns for the surface waters only.

The sketch of the May 28, 1974, image at high tide +0.9 hour shows the flow to be predominately downstream (ebb flow). The Bailey Creek plume is seen to hug the shoreline of Bailey Bay and move downstream around Jordan Point and into a secondary channel that passes through Tar Bay. The Gravelly Run plume covers a wide area immediately at the mouth of Bailey Creek. A hook-like feature near the mouth of Gravelly Run is notable.

Figure 4 shows the sketch of plume patterns 0.80 hour later (high tide +1.7 hours) on May 28, 1974. This sketch shows a change in plume patterns caused by the ebb flow condition in the James River. An extensive movement of the Bailey Creek plume downstream, beyond Jordan Point, is evident and the Gravelly Run plume is now located across the mouth of Bailey Creek, in a more linear, shearing fashion. The hook-like feature in the previous sketch has shown evidence of downstream migration as well.

To lend support to the interpretation of the photographic images, the May 28, 1974, thermal map for the Hopewell area is presented in figure 5. The image shown is based on raw, unsmoothed multispectral scanner data which have been calibrated in an approximate manner using historical data. (Temperature measurements were not taken in Gravelly Run or Bailey Bay during the May 28, 1974, experiment.) Both previous studies[4] and Virginia State Water Control Board data indicate that the Gravelly Run discharge is approximately 10°C higher than the ambient James River water upstream of Hopewell. Figure 5 shows the thermal pattern at high tide +2.0 hours or just 0.25 hour after that shown in figure 4. The shape of the Gravelly Run plume deduced from the photographic image is very similar to that of the thermal image 0.25 hour later. The Gravelly Run plume may be distinguished with remote sensing data because of both its color and temperature contrasts with the surrounding waters.

Figure 6 is a blownup thermal image showing the Hopewell waterfront area. In this image, some smoothing was applied to the raw multispectral scanner data before the map was produced. In spite of the smoothing process, several small discharge points along the Hopewell waterfront can be observed in addition to the effluents from Gravelly Run and Bailey Creek.

Figure 7 is a sketch of the Hopewell area as imaged on February 1, 1974, at high tide +3.7 hours near maximum ebb flow conditions. Although the river flow conditions and winds are changed from those on May 28, 1974, (table 1), the features of the flow are similar to those shown previously. The Bailey Creek plume is seen to be along the Bailey Bay shoreline, around Jordan Point, and down the secondary channel into Tar Bay. There is some evidence of plume flow into the main navigation channel of the James River. The Gravelly Run plume has much the same appearance as in figures 4 and 5.

On May 17, 1977, a long-duration experiment was conducted on the James River which included 24 overpasses of the Hopewell area by an NASA aircraft carrying both a mapping camera and a multispectral scanner. The temporal extent of this experiment is indicated on figure 1. From these photographic images, four were selected for sketches that exemplify the range of the tidal cycle included in this experiment. The river flow and wind conditions were both low on this day as noted in table 1. Figure 8 presents the conditions of high tide +6.9 hours and, in fact, is the condition of slack water after ebb. This should demonstrate the maximum downstream extent of the Bailey Creek plume just before the tide turns to flood. Because of slack water conditions, the Gravelly Run plume is seen to extend outward from shore toward the main channel. Also, the Bailey Creek plume appears to be sheared off into the main navigation channel off Jordan Point and mixed to the extent that it is not visible in the photography after entering the main channel. The plume, however, remains highly visible in the secondary channel into Tar Bay.

Figure 9 shows the condition of high tide +8.4 hours when the tide is on the flood. James River water is seen to encroach upon and move upstream around Jordan Point causing a disorganized plume appearance. The Gravelly Run plume is now seen to move upstream toward City Point and in areas, to mix with Bailey Creek plume waters.

The conditions at high tide +11.9 hours for May 17, 1977, are shown in figure 10. This corresponds also to slack water after flood and represents the probable maximum upstream extent of the plumes on this day. The Bailey Creek and Gravelly Run plumes have been nearly swept clear of Jordan Point and nearshore areas of Bailey Bay. The Bailey Creek plume is seen to extend beyond City Point and divide up between the two channels of the Appomattox and James Rivers. The Gravelly Run plume appears extended in an upstream manner and disappears into the main navigation channel of the James River.

The final sketch, figure 11, is the condition following high tide at +1.5 hours, just after the tide is on the ebb. Under these circumstances, James River waters are seen sweeping into the Gravelly Run plume and dividing the Bailey Creek plume into two parts, one of which moves up in the main navigational channel and the other around Bailey Bay and Jordan Point into the secondary channel. These features may also be seen in figure 12 which is a reproduction of the near-infrared, second-generation color transparency from which the sketch of figure 11 was made.

Of the aircraft remote sensing experiments conducted to date, the use of color infrared film appears to give the most descriptive images of the Hopewell area over a wide range of solar elevation angles and haze conditions. Details of the photographic system which was successfully used on the May 17, 1977, experiment are described in table 2.

TABLE 2.
AERIAL PHOTOGRAPHIC SYSTEM USED OVER HOPEWELL, VA. MAY 17, 1977

CAMERA AND SETTINGS
Camera - Zeiss aerial mapping Lens - 15.2 cm (6 in) Shutter speeds - 1/115 (morning mission) 1/200 (afternoon mission) F-stop - Automatic exposure control ASA number - 80 Field of view - 37 x 37 degrees
FILM AND FILTERS
Film - Kodak 2443 Film format - 22.9 x 22.9 cm (9 x 9 in) Emulsion number - Kodak 206-2 Filter 1 - KLF 36 Filter 2 - Wratten 12 (minus blue-haze reduction)
AIRCRAFT ALTITUDE - 3270 m (10,730 ft)
AIRCRAFT SPEED - 138 m/sec (268 knots)
IMAGE OVERLAP - 60 percent

It is believed that this system might be useful to other agencies for monitoring activities in the Hopewell area, particularly if rapid response capabilities are required.

CONCLUDING REMARKS

The National Aeronautics and Space Administration is investigating the potential of remote sensing for the monitoring of various water quality parameters in cooperation with the Environmental Protection Agency. Over the past several years, some 30 overflights of the Hopewell area have been conducted. Results indicate that surface-water plume patterns may be observed with photographic and thermal remote sensing systems. Long-duration experiments over a significant portion of the tidal cycle provide information on hydraulic characteristics which may aid scientific understanding and analytical modeling of pollutant transport. Multispectral scanner data of the Hopewell area, not processed at the present time, may enable definition of further details concerning river hydraulics and industrial discharge plume characteristics.

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2. 1974 Water Resources Data for Virginia. USGS, Richmond, Virginia, 1974.

3. Johnson, R. W.; Batten, C. E.; Bowker, D. E.; Bressette, W. E.; and Grew, G. W.: Preliminary Data from the May 28, 1974, Simultaneous Evaluation of Remote Sensors Experiment. NASA TM X-72676, June 1975.

4. Bloom, S. G.; Birch, T. J.; and Raines, G. E.: The Effect of the Thermal Discharge from the Hopewell Chemical Plant on Bailey Bay. Battelle Columbus Laboratories, May 1972.

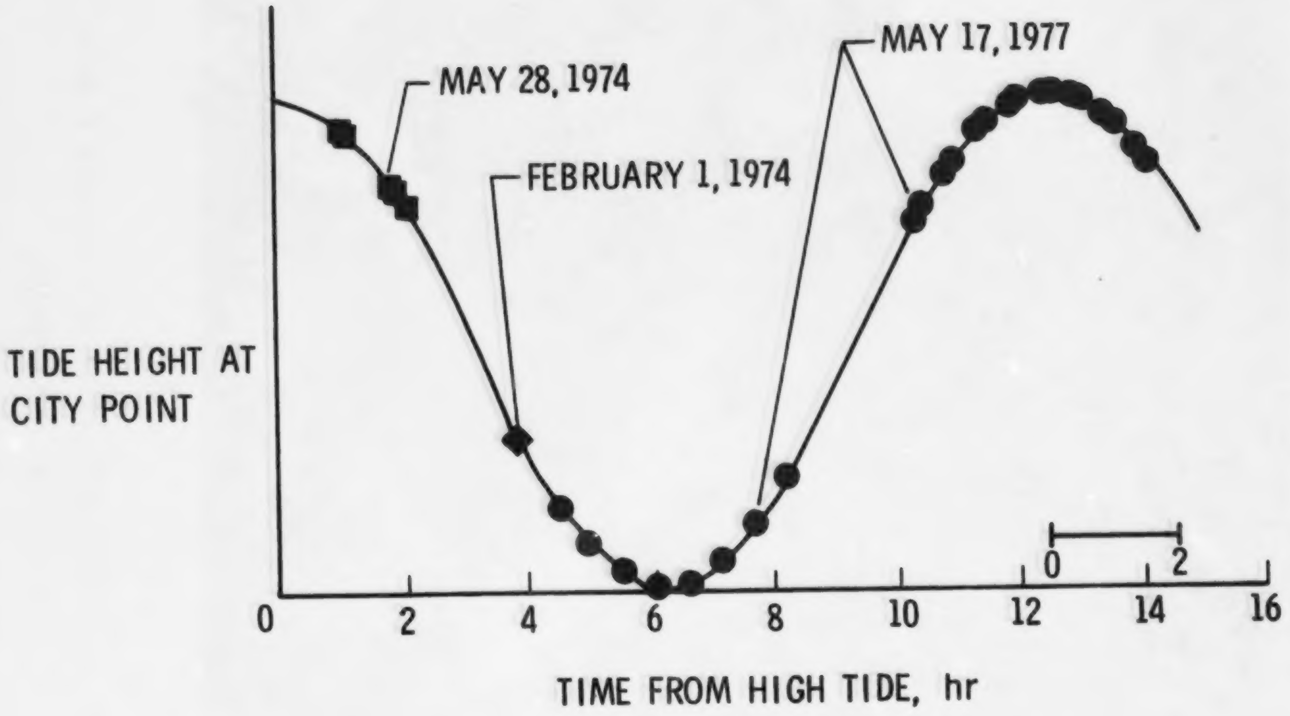


Figure I. - Tides at time of remote sensor overpass for Hopewell, Virginia.

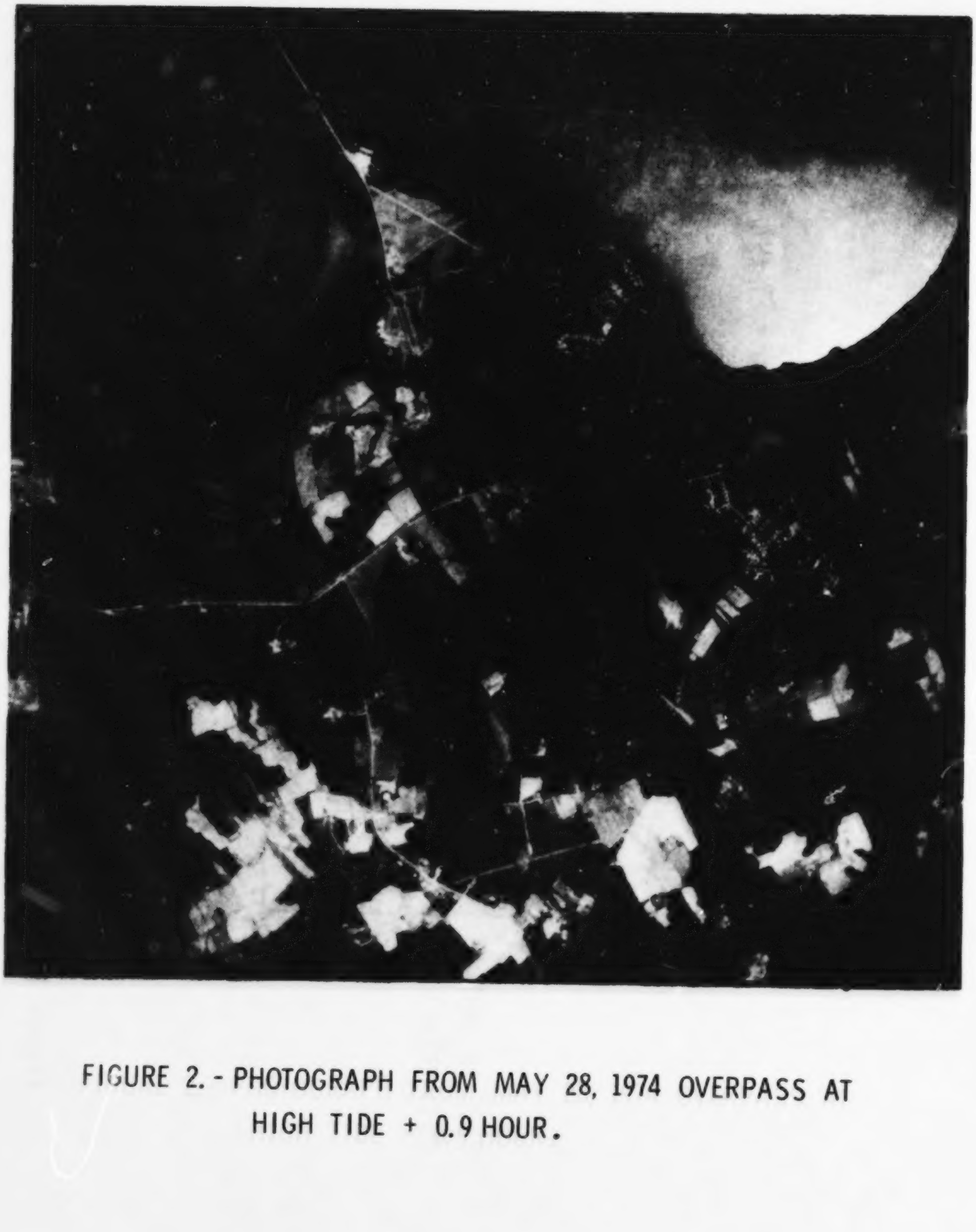
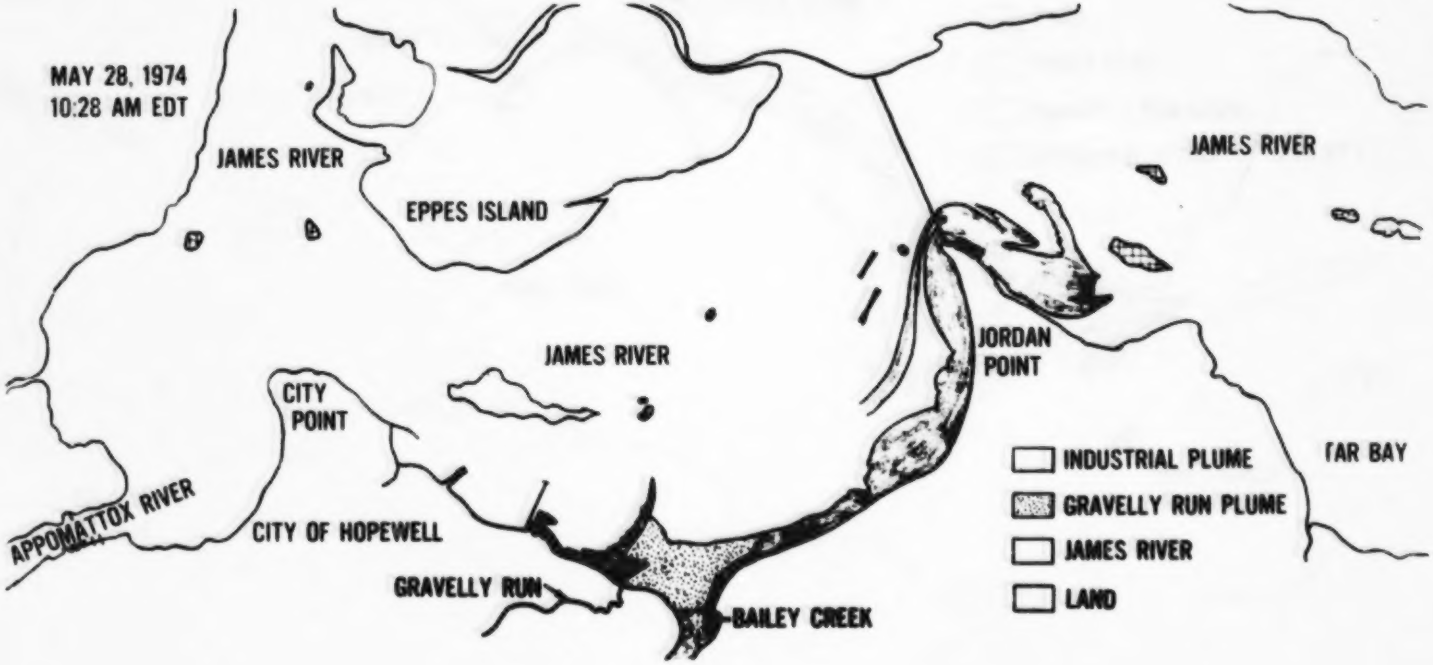


FIGURE 2. - PHOTOGRAPH FROM MAY 28, 1974 OVERPASS AT HIGH TIDE + 0.9 HOUR.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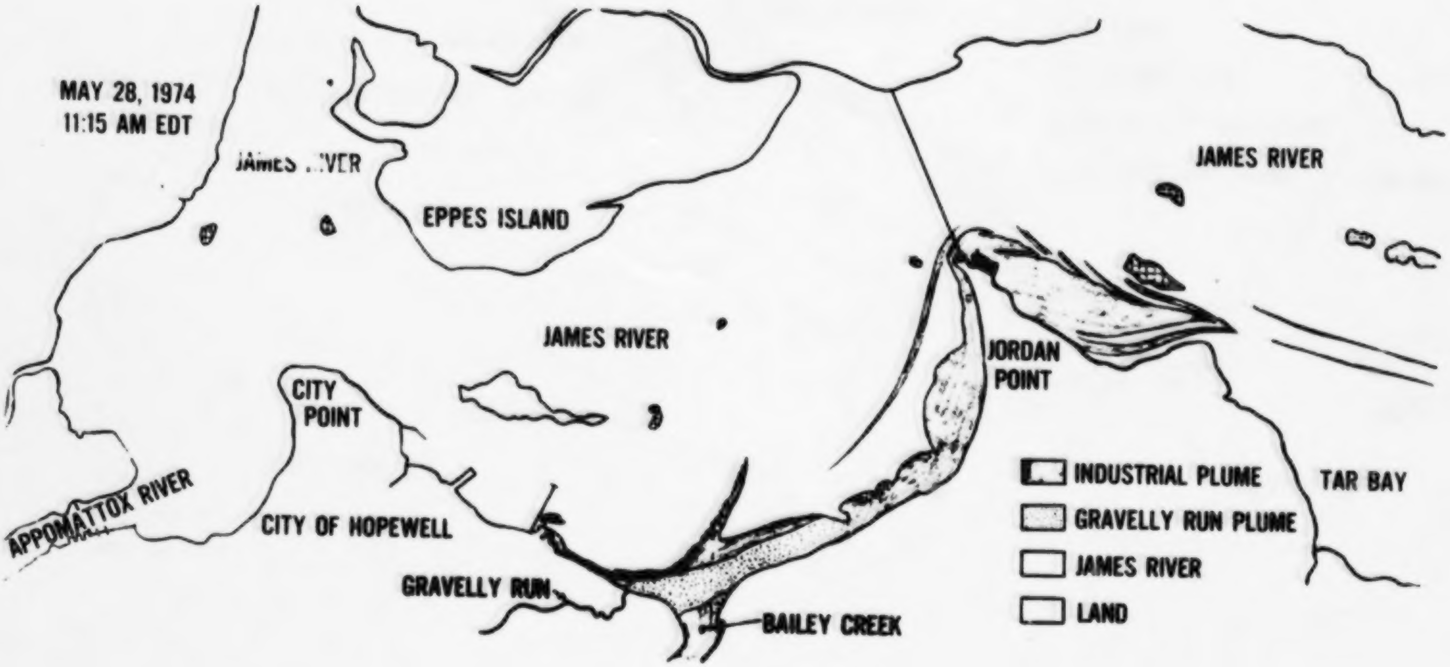
EPPES ISLAND
JAMES RIVER
JAMES RIVER
JORDAN POINT
CITY POINT
APPOMATTOX RIVER
CITY OF HOPEWELL
GRAVELLY RUN
BAILEY CREEK
TAR BAY
☐ INDUSTRIAL PLUME
▨ GRAVELLY RUN PLUME
☐ JAMES RIVER
☐ LAND

Figure 3. - Sketch of plumes at high tide +0.9 hour, May 28, 1974.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JAMES RIVER
JAMES RIVER
CITY POINT
CITY OF HOPEWELL
APPOMATTOX RIVER
GRAVELLY RUN
BAILEY CREEK
JORDAN POINT
TAR BAY
INDUSTRIAL PLUME
GRAVELLY RUN PLUME
JAMES RIVER
LAND

Figure 4. - Sketch of plumes at high tide +1.7 hours, May 28, 1974.

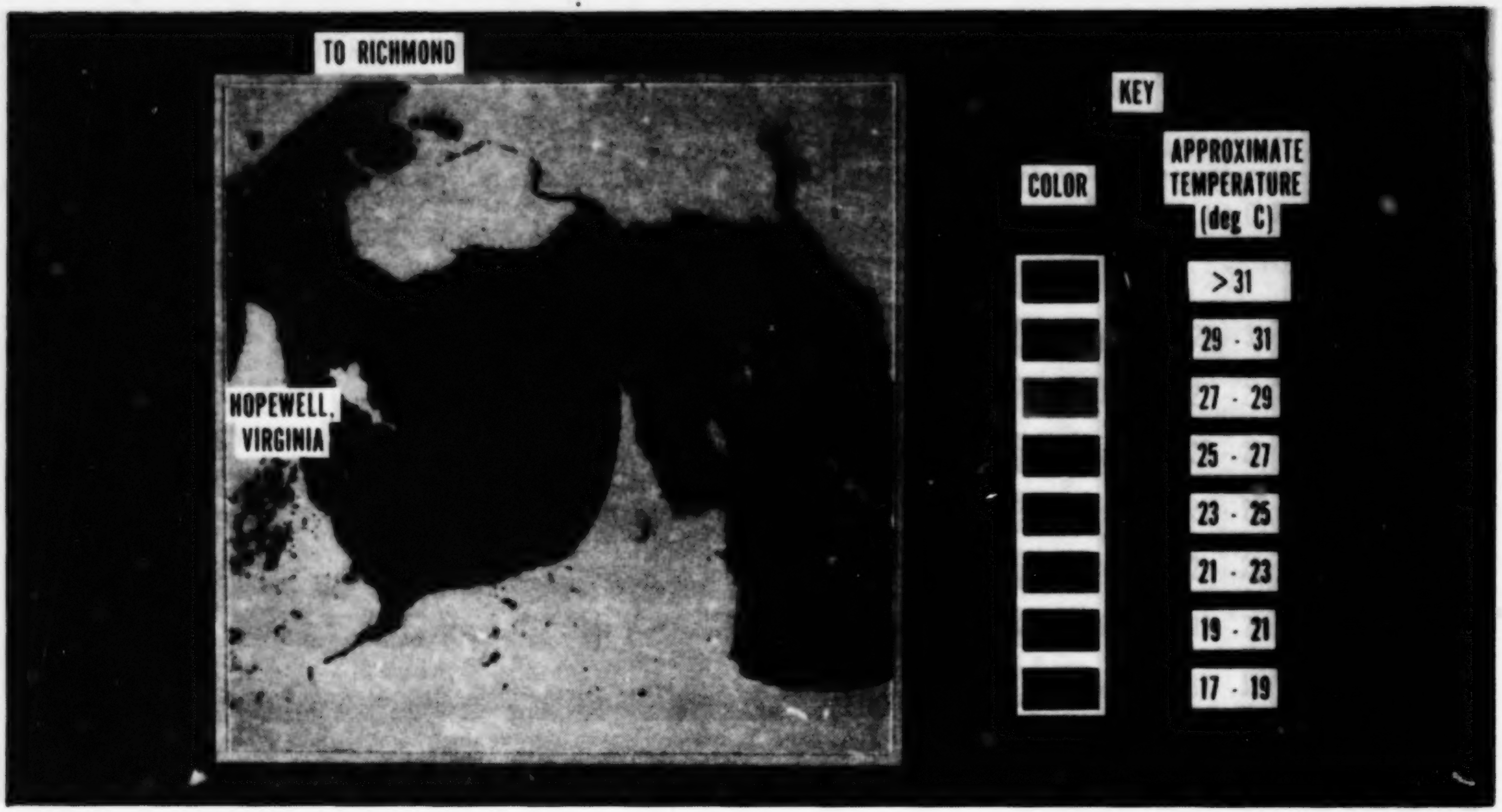

TO RICHMOND
HOPEWELL, VIRGINIA
KEY
COLOR
APPROXIMATE TEMPERATURE (deg C)
>31
29 - 31
27 - 29
25 - 27
23 - 25
21 - 23
19 - 21
17 - 19

Figure 5. - Temperature distribution in James River at high tide +2.0 hours, May 28, 1974.

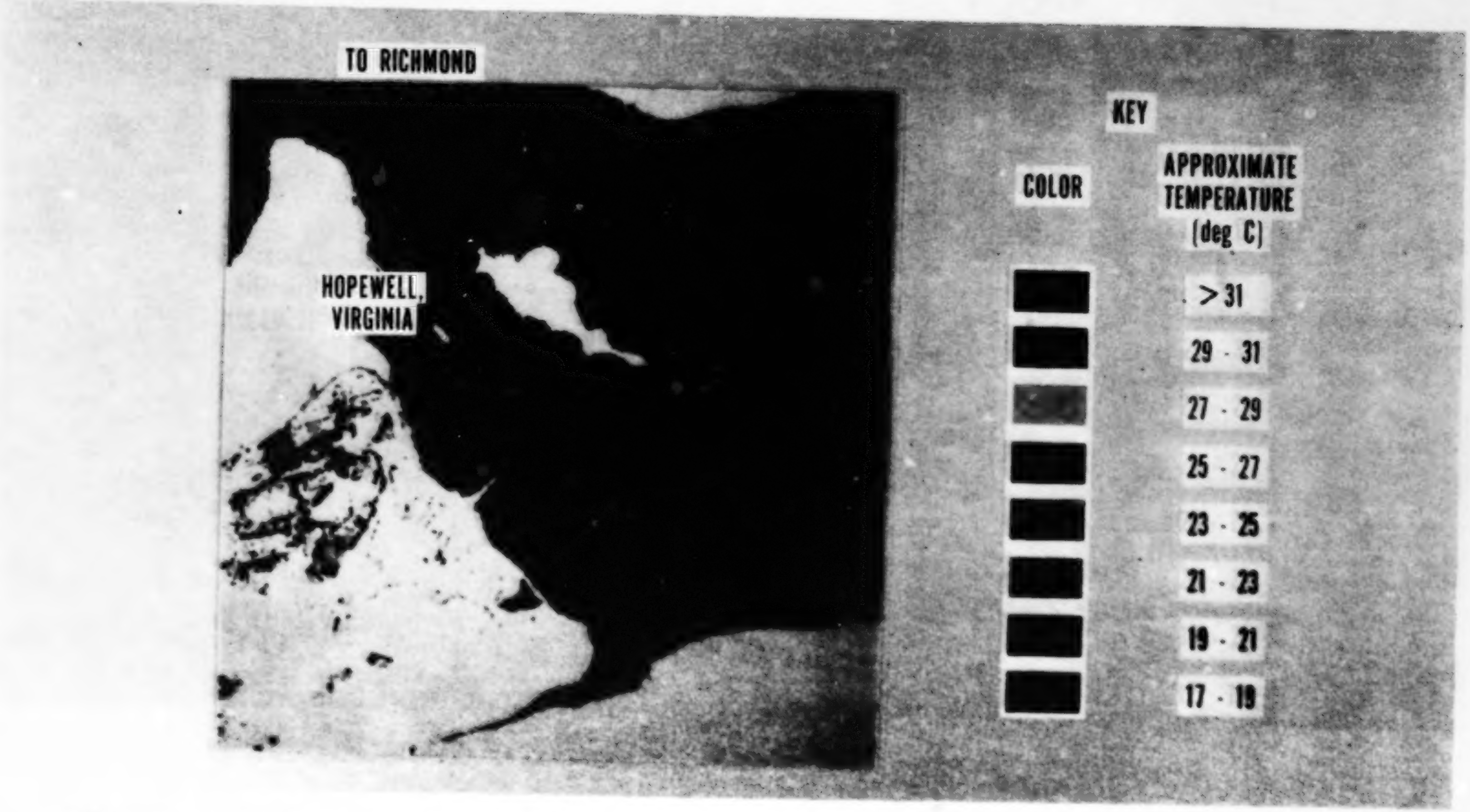

TO RICHMOND
HOPEWELL, VIRGINIA
KEY
COLOR
APPROXIMATE TEMPERATURE (deg C)
>31
29 - 31
27 - 29
25 - 27
23 - 25
21 - 23
19 - 21
17 - 19

Figure 6. - Temporature distribution along Hopewell waterfront at high tide +2.0 hours, May 28, 1974.

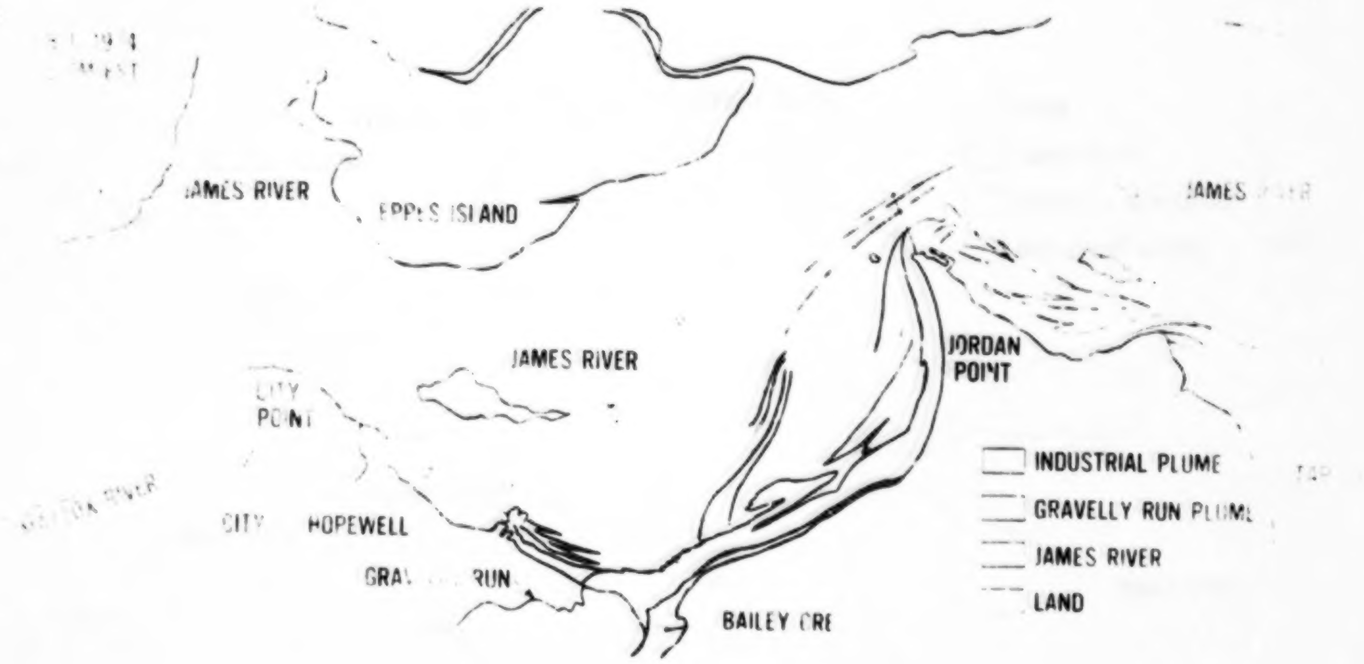
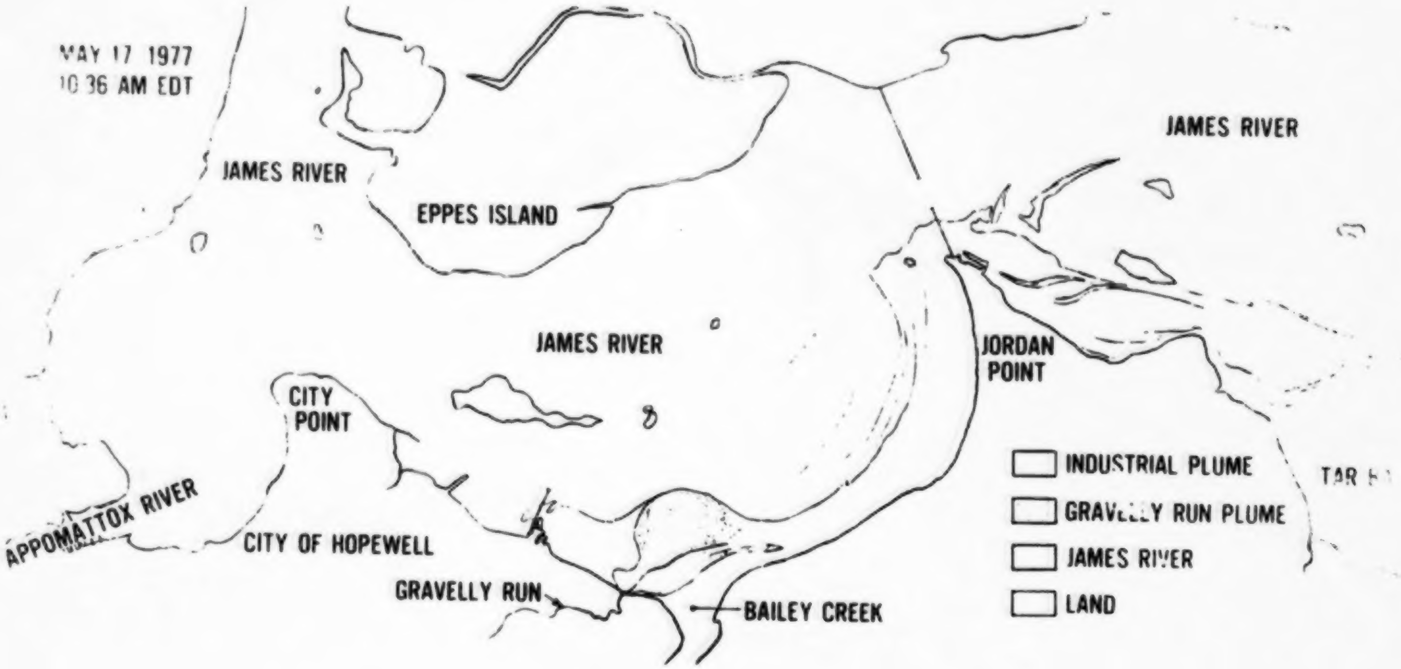

JAMES RIVER
EPPES ISLAND
JAMES RIVER
JAMES RIVER
CITY POINT
CITY
HOPEWELL
GRAV RUN
BAILEY CRE
JORDAN POINT
INDUSTRIAL PLUME
GRAVELLY RUN PLUME
JAMES RIVER
LAND

Figure 7. - Sketch of plumes at high tide +3.7 hours, February 1, 1974.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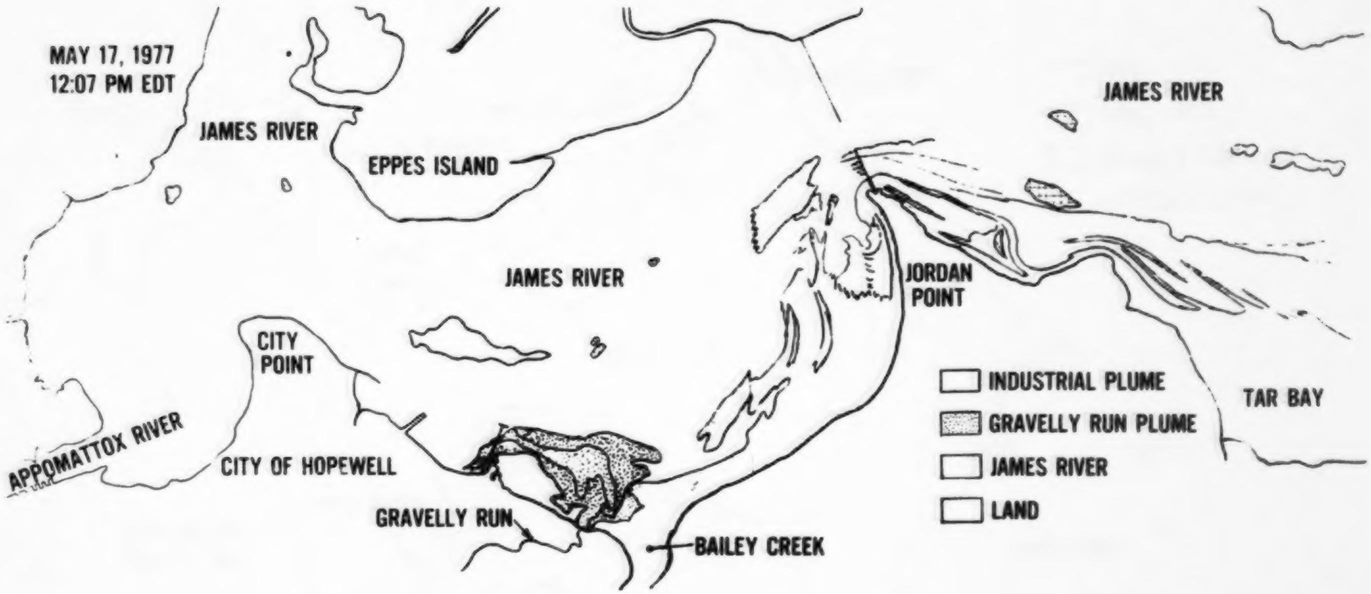
EPPES ISLAND
JAMES RIVER
JAMES RIVER
CITY POINT
APPOMATTOX RIVER
CITY OF HOPEWELL
GRAVELLY RUN
BAILEY CREEK
JORDAN POINT
INDUSTRIAL PLUME
GRAVELLY RUN PLUME
JAMES RIVER
LAND
TAR

Figure 8. - Sketch of plumes at high tide +6.9 hours, May 17, 1977.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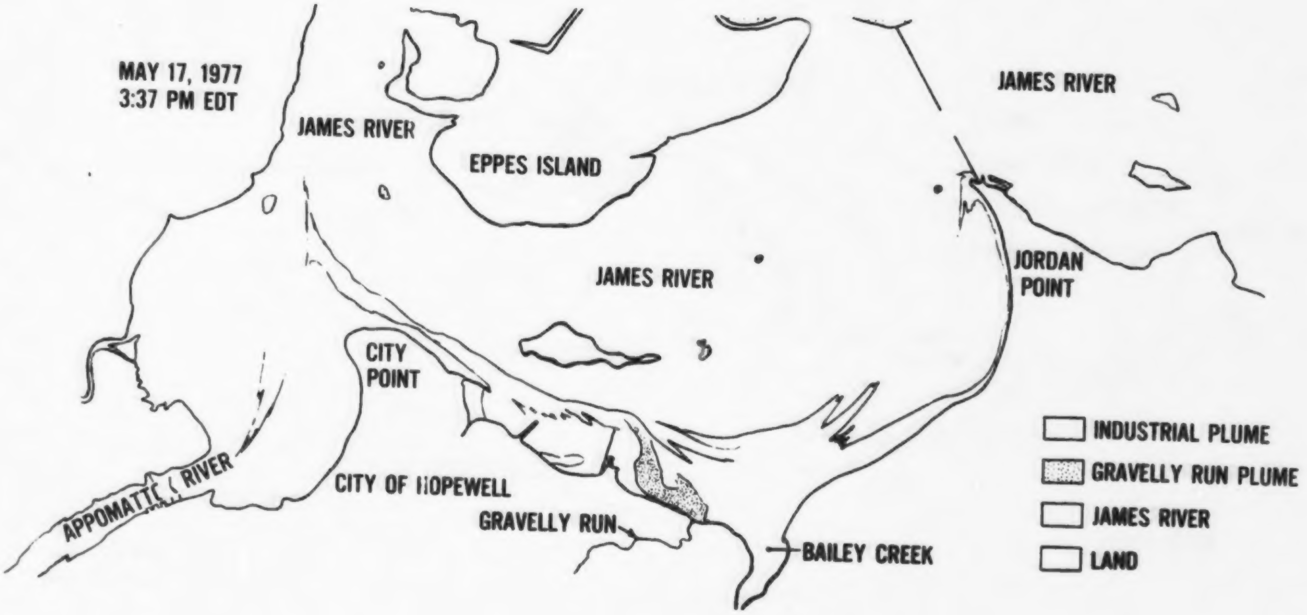
JAMES RIVER
JORDAN POINT
CITY POINT
APPOMATTOX RIVER
CITY OF HOPEWELL
GRAVELLY RUN
BAILEY CREEK
TAR BAY
☐ INDUSTRIAL PLUME
▨ GRAVELLY RUN PLUME
☐ JAMES RIVER
☐ LAND

Figure 9.- Sketch of plumes at high tide +8.4 hours, May 17, 1977.



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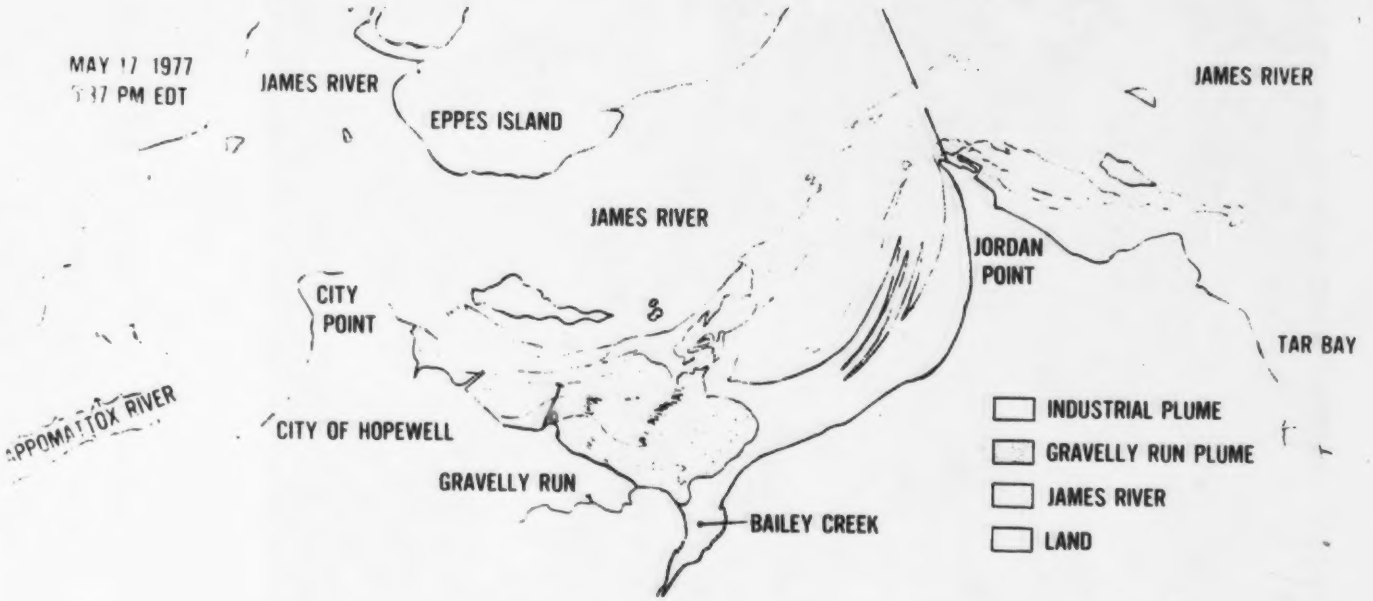
JAMES RIVER
JAMES RIVER
JORDAN POINT
CITY POINT
CITY OF HOPEWELL
GRAVELLY RUN
BAILEY CREEK
APPOMATTOX RIVER
INDUSTRIAL PLUME
GRAVELLY RUN PLUME
JAMES RIVER
LAND

Figure 10. - Sketch of plumes at high tide +11.9 hours, May 17, 1977.



MAY 17 1977
5:37 PM EDT
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EPPES ISLAND
JAMES RIVER
JAMES RIVER
JORDAN POINT
TAR BAY
CITY POINT
APPOMATTOX RIVER
CITY OF HOPEWELL
GRAVELLY RUN
BAILEY CREEK
☐ INDUSTRIAL PLUME
☐ GRAVELLY RUN PLUME
☐ JAMES RIVER
☐ LAND

Figure 11. - Sketch of plumes at high tide +13.9 hours (+1.5 hours), May 17, 1977.

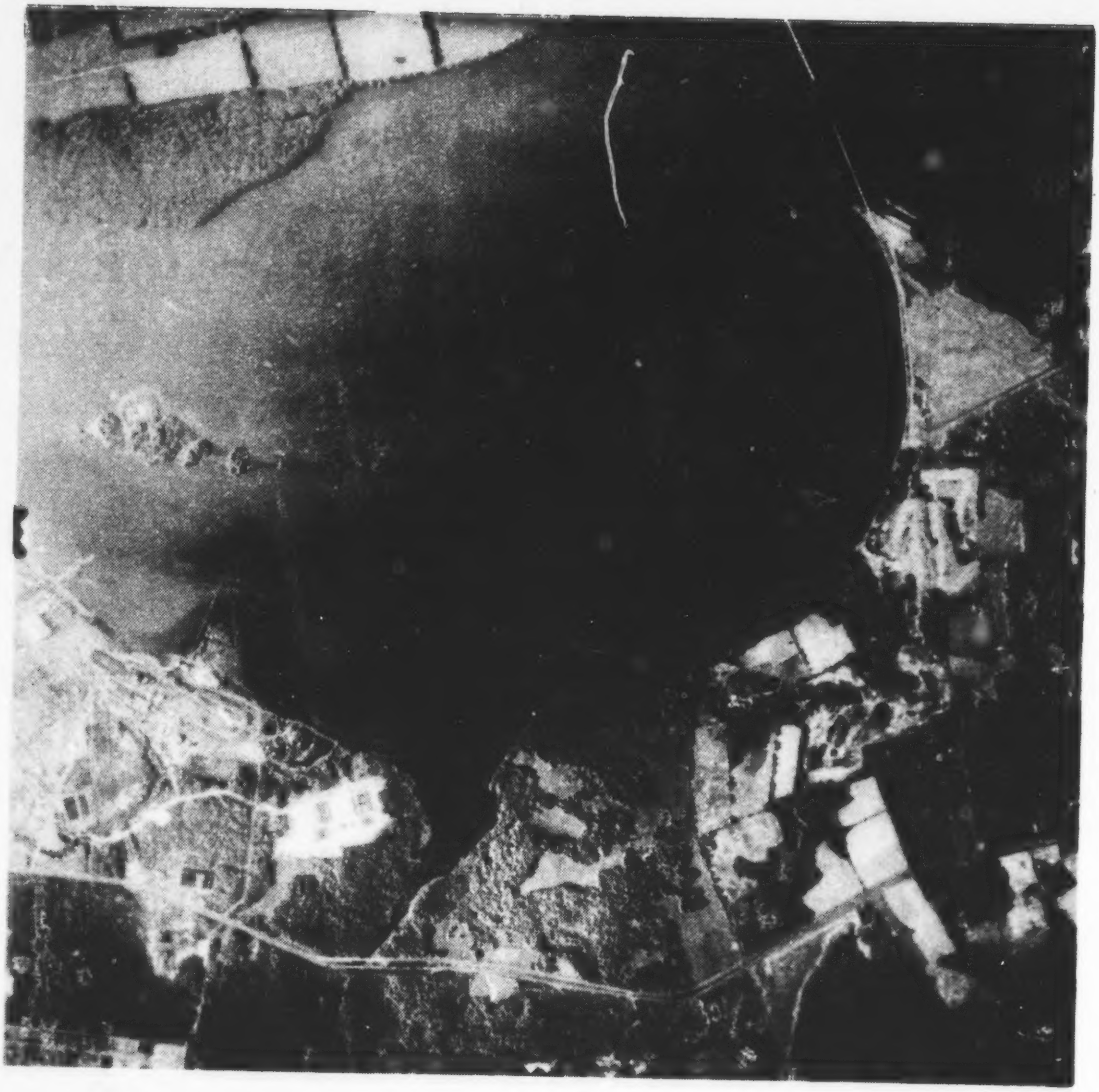

FIGURE 12. - PHOTOGRAPH FROM MAY 17, 1977 OVERPASS AT HIGH TIDE + 1.5 HOURS.

ALLIED CHEMICAL KEPONE INVESTIGATIONS

A. R. Paterson, R. J. Williams, D. E. Scheirer, J. Vitrone

Two investigations have been in progress during the past year at Allied Chemical in Morristown, NJ that seem to offer some promise in relation to the Kepone problem. One approach offers a possible means of immobilization of the material in the James River. The second presents a means of destruction for Kepone residues of varying concentrations.

The first investigation was initiated after we observed early in the year that the majority of the Kepone in the river was associated with the organic material in the bottom sediment. We decided at that point to attempt addition of small particles of coal as a means of adsorbing Kepone and decreasing its availability.

Early experiments indicated that Kepone is removed from solution by coal and that the removal, though not rapid, continues for at least 28 days. At that point we found that the Kepone concentration had been decreased by 70%.

The data are as follows:

Initial Kepone Concentration	Particle Size	Time	% Reduction	Stirring
96 ppb	-8, +14 mesh	4 days	24%	3 hours
96 ppb	-8, +14 mesh	12 days	35%	3 hours
1.9 ppb	-8, +14 mesh	15 minutes	20%	15 minutes
1.9 ppb	-8, +14 mesh	3 hours	40%	3 hours
1.9 ppb	-8, +14 mesh	1 day	55%	1-1/2 hours
1.9 ppb	-8, +14 mesh	7 days	65%	1-1/2 hours
1.9 ppb	-8, +14 mesh	15 days	72%	1-1/2 hours

Further work with coal in the presence of Kepone containing sediment indicated that the level of dissolved Kepone decreased by about 50%, when a thin layer of coal was placed on top of the soil. The procedure and results are as follows:

Procedure

Approximately 21-23 g (dry wt) of James River bottom soil (Buoy #107) was added to a 60 OD X 142 mmL centrifuge bottle. The amount of soil was matched to within 0.3 g in a sample pair. A 1-1/2 inch Teflon stir bar was added to each centrifuge bottle followed by 95 ml of distilled water. A 5 ml aliquot from a methanolic Kepone solution (20.8 mg ^{14}C labeled Kepone dissolved in 200 ml methanol was then added to each centrifuge bottle. The Kepone was mixed with the soil by vigorous stirring for 30 minutes. Each sample pair was then centrifuged for about 30 minutes. Each sample pair was then centrifuged for about 30 minutes to rapidly settle the soil particles. The samples were usually left at rest for 1-2 days before adding the coal. About 1.5 g of -8,+14 mesh coal was added to one of the centrifuge bottles in each sample pair. The other sample (without coal) in the pair served as a control. The coal was added without any agitation of the sample. The amount of coal corresponded roughly to a monolayer of coal over the soil. After standing at rest for 1 to 12 days, each sample pair was filtered using a 0.45 Millipore filter to remove any suspended soil particles. The filtrate was then transferred to a 250 ml separatory funnel and extracted for 5 minutes with 40 ml of toluene. Four of five drops of concentrated sulfuric acid were added to the filtrate to aid in the extraction. Following the extraction, the toluene was transferred to a 50 ml volumetric flask. The Kepone content was determined by liquid scintillation using a cocktail consisting of 5 ml of toluene from the 50 ml volumetric flask and 10 mL of Insta-Gel (Packard). Results were expressed as the amount of Kepone in a 100 ml of water.

Results of experiments carried out to date are as follows:

Sample 45 with coal	22 ppb remaining in solution after 12 days	
Sample 46 without coal	42 ppb remaining in solution after 12 days	48% Reduction
Sample 49 with coal	19 ppb remaining in solution after 4 days	
Sample 50 without coal	44 ppb remaining in solution after 4 days	57% Reduction
Sample 53 with coal	37 ppb remaining in solution after 12 days	
Sample 54 without coal	50 ppb remaining in solution after 12 days	26% Reduction

Sample 57 with coal	40 ppb remaining in solution after 1 day	37% Reduction
Sample 58 without coal	63 ppb remaining in solution after 1 day	

We are hoping to run some tests in the near future with living organism to evaluate the effect of added coal on Kepone uptake.

The second investigation involves destruction of Kepone through the use of caustic solutions at elevated temperature and pressure.

Materials chosen for testing were Kepone, Mirex and three samples of clean-up wastes from the Baltimore plant. In general, samples were mixed with water to form solutions or slurries, concentrations up to about 5%, in the presence of sufficient sodium hydroxide to provide a one-half molar solution of sodium hydroxide at the completion of the reaction, and held in the presence of oxygen from two to ten minutes at temperatures of 300-350°C. Sufficient pressure, 2000 psi - 2200 psi, was applied to maintain water in the liquid state. Alkali was used to aid dehalogenation and prevent the formation of a substantial carbon dioxide gas phase.

Experimental variables have not been exhaustively explored, but conditions were found at which Kepone concentrations in the reaction product were reduced to less than the limit of detection using gas chromatography with detection by electron capture. The rate of Kepone disappearance under these conditions appears to be at least three orders of magnitude per minute. The results for Mirex were the same.

An additional goal was destruction of all organic matter in the samples. That this was achieved was evident from the chromatograms obtained in the analyses.

Our conclusions at this point are:

1. The high-temperature hydrolysis and oxidation is a technically feasible means for disposal of Kepone and Kepone-bearing wastes.

2. The procedure should have wide applicability in disposing of halogenated organics and organics in general.

3. The process would have an advantage over incineration in that, in the event of mishap, the material in process could be contained readily and recycled if decomposition were incomplete.

SUMMARY OF KEPONE SEMINAR ISSUES

by

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Washington, D.C.

The past two days' presentations and discussions have provided a comprehensive survey of much of the work related to the problem of Kepone contamination in the James River. I'll now try to place this material in perspective and describe the interrelationships. A solution to the Kepone contamination problem in the James obviously involves a full assessment of the nature and extent of the current contamination, knowledge of the effect of the contamination on human health and the environment as well as its social and economic impact, an analysis of potential mitigative measures and an eventual assessment of various action-no action alternatives. Except for the last item--assessment of various action-no action alternatives--we have heard presentations and discussion directed to all of these issues. It would serve no useful purpose now to categorize each individual presentation we have heard into the issues I have listed. However, much of the work described here today is either being utilized in, or is an integral part of the Kepone Mitigation Feasibility Project we are conducting at EPA. Our project approach has been organized to address each of the issues I have cited. Therefore a discussion of the project itself may be the most useful way to place the types of efforts discussed here in perspective. A few background facts may be helpful.

The Governors of Virginia and Maryland, in the Fall of 1976, jointly requested that EPA evaluate the Kepone contamination of the James River and its tributaries, and explore corrective or mitigative actions. In response to this request, a two-phased project plan was adopted. Phase I involves a detailed assessment of: (1) suspected continuing sources of Kepone contamination; (2) the fate and transport of Kepone in the James River system; (3) the current and long-range effects of Kepone contamination on the biota; and (4) an evaluation of mitigation and removal methods. The results of Phase I are to provide a basis for action recommendations. Following a review of the Phase I recommendations by EPA and the States of Virginia and Maryland, Phase II may involve a decision to: seek funding for a major cleanup or mitigation program; proceed with pilot testing of alternative corrective and mitigative actions; or withhold action due to unfavorable cost/benefit assessments.

An allocation of $1.4 million was made for the Phase I effort. A comprehensive work plan was developed and support studies were arranged with the U.S. Army Corps of Engineers, the Energy Research and Development Agency (ERDA), the EPA Gulf Breeze, Florida, Environmental Research Laboratory, and the Virginia Institute of Marine Science. Engineering studies to contain, stabilize, or remove Kepone-contaminated sediments have been conducted and eighteen alternatives to mitigate the Kepone problem have been evaluated. In addition, the Corps has contracted with the U.S. Fish and Wildlife Service to investigate the wetland ecosystem to compare plant and animal distribution patterns with unaffected areas.

Under the interagency agreement with ERDA, the ERDA/Battelle Pacific Northwest Laboratories are: (1) conducting sampling and analysis of the suspected sources of Kepone contamination into the James River; (2) obtaining in cooperation with the Virginia Institute of Marine Science, water quality, sediment, hydrological and other data on the James River; (3) modelling the transport and fate of sediments in the river; (4) evaluating nonconventional Kepone mitigation techniques; and (5) assessing the ecological impact of the current Kepone contamination and possible mitigation approaches. The EPA Gulf Breeze Laboratory provided scientific data and analysis on the effect of Kepone on the estuarine biota, including biological accumulation, plus distribution and fate of Kepone. The Virginia Institute of Marine Science is collecting field data on the James River. Results of these investigations are being integrated into models of Kepone movement and sediment transport by Gulf Breeze and ERDA/Battelle Laboratories, respectively. The final report describing the results of these investigative efforts will be completed in March 1978, and will be the basis for considering the Phase II efforts.